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SOLUBILITY OF ALKALI METAL AMIDES IN ALIPHATIC AMINES

BY



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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "SOLUBILITY OF ALKALI METAL AMIDES IN ALIPHATIC AMINES" submitted by Toshiyuki Ishige in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

ABSTRACT

This thesis presents the results of an experimental investigation of the preparation and solubility in amines of certain potassium and lithium amides which may be effective catalysts for the exchange of deuterium between hydrogen and aliphatic amines. The amines selected for study were methylamine, propylamine, pyrrolidine, 1,2-propanediamine and 1,3-propanediamine.

Experimental techniques were developed and checked by measuring the solubility of potassium amide in liquid ammonia at -77°C and comparing the results with those published in the literature. Then other amides of interest were prepared and solubility measurements made at -77°C or at room temperature.

Lithium dissolved in all the amines studied. Potassium dissolved in methylamine and in the diamines but did not dissolve appreciably in propylamine and pyrrolidine. The alkali metal solutions were dark blue and they decomposed by the reaction of the dissolved metal with the amine to form amide solutions.

The times required to dissolve the metal and for the completion of the reaction differed for different metals and for different amines; some within several hours, some over several days. Generally lithium dissolved and reacted faster than potassium and the amides of lithium



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were more soluble. Ferric oxide was employed as a catalyst to enhance the rate of reaction for some of the systems studied.

Potassium amide was found to be slightly soluble in all the amines studied.

The amine solutions of amides were colorless or pale yellow. These solutions were very sensitive to oxygen and quickly turned dark brown upon exposure to the atmosphere.

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TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
1. INTRODUCTION	1
2. LITERATURE REVIEW	4
2-1 Classification and Nomenclature of Amines and Amides	4
2-2 Properties of Amines and Their Nature as Acids and Bases	8
2-3 Properties and Handling of Alkali Metals and Alkali Metal Amides	13
2-4 Preparation and Solubility of Potassium Amide	20
2-5 Solubility of Alkali Metals in Aliphatic Amines	29
2-6 Preparation and Solubility of Aliphatic Alkali Amides	32
3. EXPERIMENTAL	36
3-1 Equipment	36
3-2 Materials	39
3-3 Experimental Procedures	42
(A) Purification of Amines	42
(B) Amide Preparation	43
(C) Sampling	44
(D) Analysis	44
3-4 Experimental Results	46
(A) Solubility of Potassium Amide in Liquid Ammonia	46
(B) Solubility of Potassium in Methylamine	51
(C) Solubility of Lithium in Methylamine	53
(D) Solubility of Potassium Amide in Methylamine	56

(E) Solubility of Lithium Amide in Methylamine	58
(F) Solubility of Potassium in Propylamine	58
(G) Solubility of Lithium in Propylamine	58
(H) Solubility of Potassium Amide in Propylamine	60
(I) Solubility of Lithium Amide in Propylamine	62
(J) Solubility of Potassium in Pyrrolidine, 1,2-Propanediamine and 1,3-Propanediamine	62
(K) Solubility of Lithium in Pyrrolidine	63
(L) Solubility of Lithium in 1,2-Propanediamine	64
(M) Solubility of Lithium in 1,3-Propanediamine	65
(N) Solubility of Potassium Amide in Pyrrolidine, 1,2-Propanediamine and 1,3-Propanediamine	66
4. DISCUSSION	69
4-1 Equipment	69
4-2 Purification of Amines	70
4-3 Reaction of Alkali Metal with Amines	71
4-4 Color Phenomena	72
4-5 Accuracy of Data and Comparison with Data Reported in the Literature	74
5. CONCLUSIONS	79
BIBLIOGRAPHY	81
APPENDIX 1 Calculations Involved in Titration	85
APPENDIX 2 Density of Liquid Ammonia	87

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	The IUPAC Names for Amines	5
2	A List of Names of Metal Amides of Amines	7
3	A summary of Amine Properties	11
4	Chemical Properties of Alkali Metals	16
5	Physical Constants of Alkali Amides	19
6	A List of Materials and Their Source	40
7	Amine Purity and Major Impurities	41
8	A Summary of Solubility Study	47
9	Measured Solubility of KNH_2 in Ammonia	50
10	Measured Solubility of CH_3NHK in Methylamine	53
11	Measured Solubility of CH_3NHLi in Methylamine	55
12	Measured Solubility of KNH_2 in Methylamine	57
13	Measured Solubility of KNH_2 in Propylamine	61

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Solubility Diagram of Potassium Amide in Ammonia	28
2	Schematic Drawing of Equipment	37
3	Reaction Vessel and Sampling Unit	38
4	Color Photograph of Potassium in Methylamine	77
5	Color Photograph of Powdered Lithium in Propylamine	77
6	Color Photograph of Lithium in 1,2-Propanediamine	77
7	Color Photograph of Lithium in 1,3-Propanediamine	78
8	Color Photograph of Potassium Amide in 1,3-Propanediamine	78
9	Density of Liquid Ammonia	88

1. INTRODUCTION

Demand for heavy water as a moderator in nuclear power plants is sharply increasing because the heavy water moderated reactor is becoming competitive with conventional thermal power plants for generating electricity (1,2). In fact, it has been estimated that over 2,700 tons of the heavy water will be required in Canada alone by 1973, whereas present production capacity in the world is only about 220 tons per year excluding China and Russia (2). Plants are being built in Nova Scotia in Canada and they will give an additional capacity of 800 tons per year by 1970 (3).

At present, the only existing process for producing heavy water on a large scale is the GS process (Girdler Sulphide process) (4) which is based on the isotopic exchange reaction between water and hydrogen sulphide at two different temperatures. However, the process based on deuterium exchange between ammonia and hydrogen catalyzed by potassium amide is said to be the first competitive process to the GS process (2). France is the first country to utilize this process to produce 28 tons of the heavy water per year based on ammonia synthesis gas feed (5). The main advantage of the ammonia - hydrogen exchange over the water - hydrogen sulphide exchange is that a larger separation factor is available because the system can be operated at

temperatures down to -77°C (2,5). However, the ammonia - hydrogen exchange requires an effective catalyst whereas the water - hydrogen sulphide exchange proceeds without the use of a catalyst (4,6).

A closely related process, aliphatic amine - hydrogen exchange offers a possible advantage over the ammonia - hydrogen exchange as the basis for a process for the commercial production of heavy water (2). Since the amines have lower vapor pressures, plant construction costs and energy requirements should be lower. The suitability of a particular exchange reaction for the concentration of deuterium depends upon the rate at which the reaction occurs and upon the value of the equilibrium constant for the reaction. Bar-Eli and Klein's work (7) is the only published information on the amine - hydrogen exchange. They observed that the rate of exchange of deuterium in methylamine and ethylamine is from five to thirty times faster than that in ammonia. The separation factors are thought to be equivalent to those for the ammonia - hydrogen exchange.

In the same way that the ammonia - hydrogen exchange is catalyzed by alkali metal amides, in particular potassium amide, the amine - hydrogen exchange is catalyzed by the alkali-substituted amide of a corresponding amine (7). However, knowledge on the nature of the alkali metals in amines

is very limited and most of the previous studies are only qualitative. Since liquid ammonia is a very important medium as a non-aqueous solvent, rather extensive investigations have been made on the solution of alkali metals in liquid ammonia (8,9,10,11). All the alkali metals are known to dissolve in liquid ammonia and some information is available on reactions to form amides.

Little information is available on the solubility of alkali metals and alkali metal amides in aliphatic amines. Since the alkali metal amides are potential catalysts for amine - hydrogen exchange reactions, information on their preparation, handling and solubility in amine is requisite to exchange studies which employ the amide as catalyst. The study reported herein was initiated to obtain such information.

This study has been limited to an investigation of the solubility of potassium and lithium amides in the following amines; methylamine, propylamine, pyrrolidine, 1,2-propanediamine and 1,3-propanediamine. Some solubility studies in ammonia are included for comparison purposes.

2. LITERATURE REVIEW

2-1 Classification and Nomenclature of Amines and Amides

Amines are alkyl or aryl substitution products of ammonia. Classification is made according to the number of the hydrogen atoms replaced by alkyl or aryl groups. Thus there are three types of amines, known as primary, secondary and tertiary amine. The general formulae of these three types are given below along with some examples.

Primary amine: RNH_2

CH_3NH_2 (Methylamine), $\text{H}_2\text{N}\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (1,3-Propanediamine), $\text{C}_6\text{H}_5\text{NH}_2$ (Phenylamine)

Secondary amine: $\begin{array}{c} \text{R}_1 \backslash \\ \text{NH} \\ \text{R}_2 / \end{array}$

$(\text{C}_2\text{H}_5)_2\text{NH}$ (Diethylamine), $\begin{array}{c} \text{CH}_2-\text{CH}_2 \backslash \\ | \\ \text{CH}_2-\text{CH}_2 / \end{array} \text{NH}$ (Pyrrolidine)

Tertiary amine: $\begin{array}{c} \text{R}_1 \backslash \\ \text{R}_2 - \text{N} \\ \text{R}_3 / \end{array}$

$(\text{CH}_3)_3\text{N}$ (Trimethylamine), $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ (N,N-Dimethylphenylamine)

The division of the amines into these classes is important because their chemical behaviour differs markedly with a change in state of the nitrogen atom.

Amines are named as alkyl or aryl substituted ammonia, the word "ammonia" being contracted to "amine". However, they are sometimes called derivatives of amino substituted compounds. The characteristic functional group of primary amines, -NH_2 , is called "amino". Many heterocyclic compounds have acquired trivial names over the years and they are quite unlikely to be replaced by more systematic names. Thus, more than one name is often used for the same compound. To clarify this situation, the IUPAC system of nomenclature for organic compounds (12) is used in this thesis for naming the amines. Table 1 lists the IUPAC names for the amines studied, together with their chemical formulae and currently used synonyms.

Table 1
The IUPAC Names for Amines

<u>IUPAC name</u>	<u>Formula</u>	<u>Synonyms</u>
Methylamine	CH_3NH_2	Aminomethane
Propylamine	$\text{C}_3\text{H}_7\text{NH}_2$	n-Propylamine 1-Aminopropane
1,2-Propanediamine	$\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CHNH}_2\cdot\text{CH}_3$	1,2-Diaminopropane propylenediamine
1,3-Propanediamine	$\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$	1,3-Diaminopropane Trimethylenediamine
Pyrrolidine	$ \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \quad \text{NH} \end{array} $	

Generally, amides are organic compounds having an acyl group attached to an amino nitrogen atom. However, a compound in which one of the hydrogen atoms in ammonia is replaced by a metal is also called amide, such as potassium amide, KNH_2 . All the amides that appear in this thesis belong to the latter type. The IUPAC nomenclature for inorganic compounds (13) gives the name "amide" for the $-\text{NH}_2$ group and "imide" for the $-\text{NH}$ group when they behave as anions.

The metal amide of simple amines has been named as an alkyl or aryl derivative of the parent compound MNH_2 in several references (7,14,15,16,17). These are followed in this thesis. Table 2 lists the names of the metal amides of the amines studied in this thesis.

Table 2

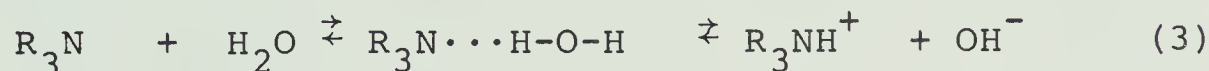
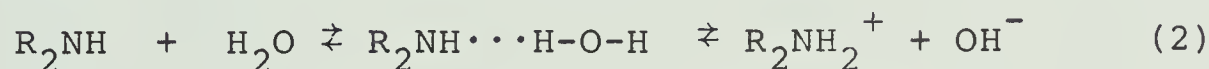
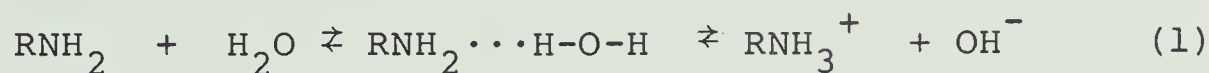
A List of the Names of Metal Amides of Amines

CH_3NHK	Potassium methylamide
CH_3NHLi	Lithium methylamide
$\text{C}_3\text{H}_7\text{NHK}$	Potassium propylamide
$\text{C}_3\text{H}_7\text{NHLi}$	Lithium propylamide
$\text{KHN} \cdot \text{CH}_2 \cdot \text{CH}(\text{NHK}) \cdot \text{CH}_3$	Dipotassium 1,2-propanediamide
$\text{LiHN} \cdot \text{CH}_2 \cdot \text{CH}(\text{NHLi}) \cdot \text{CH}_3$	Dilithium 1,2-propanediamide
$\text{KHN} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHK}$	Dipotassium 1,3-propanediamide
$\text{LiHN} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHLi}$	Dilithium 1,3-propanediamide
$ \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \diagup \\ \text{CH}_2 - \text{CH}_2 \quad \text{NK} \end{array} $	Potassium pyrrolidine
$ \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \diagup \\ \text{CH}_2 - \text{CH}_2 \quad \text{NLi} \end{array} $	Lithium pyrrolidine

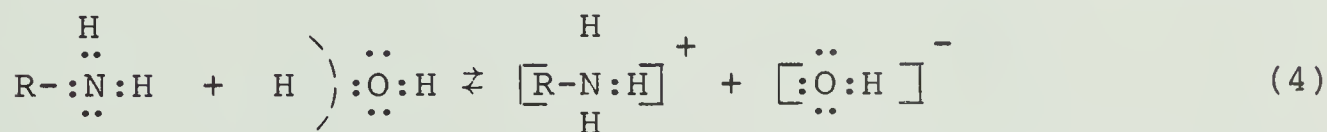
2-2 Properties of Amines and Their Nature as Acids and Bases

The simple aliphatic amines closely resemble ammonia. They are colorless gases or volatile liquids with a strong ammoniacal but somewhat fishy odor. The boiling point rises with increasing molecular weight while the odor becomes fainter. Primary amines boil at higher temperatures than the comparable secondary amines having the same number of carbon atoms, and tertiary amines have the lowest boiling points. The volatility of the primary and secondary amines is very low compared with the paraffin hydrocarbons, owing to the ability of the amines to form hydrogen bonds, $\text{N-H}\cdots\text{N}$, and thereby undergo molecular association. In general, $\text{N-H}\cdots\text{N}$ bonds are somewhat weaker than those of corresponding types, $\text{O-H}\cdots\text{O}$, $\text{F-H}\cdots\text{F}$, because the electronegativity of nitrogen is less than that of oxygen or fluorine. Thus the amines have lower boiling points than the corresponding alcohols. Tertiary amines, lacking the necessary hydrogen atom attached to nitrogen, can not undergo association and have boiling points close to comparable paraffin hydrocarbons. On the other hand, amines have a greater affinity for water than have alcohols, and their solubility in water is consequently greater.

The most characteristic chemical property of amines is their ability to act as bases by accepting protons from a variety of acids. Simple aliphatic amines, especially those of low molecular weight are bases strong enough to absorb carbon dioxide from the air forming carbonates. In comparison with sodium hydroxide, however, they are only weak bases, owing to the fact that the following equilibria, which incorporate a hydrogen bonded intermediate, lie well to the left-hand side.



These equilibria are induced by a lone pair in the octet of the electrons around the nitrogen atom which can form a dative covalency with a hydrogen atom in a water molecule.



However, it should not be forgotten that primary and secondary amines are also able to act as acids, though very weak. The lithium salts of such amines are readily prepared in ether solution by treatment of amines with phenyllithium.



The amines of interest for amine - hydrogen exchange processes must have low vapor pressures, low freezing points, and have a relatively large amount of exchangeable hydrogen per unit molecular weight. Thus tertiary amines are excluded from our study. A summary of the physical properties of the five amines selected for catalyst solubility study is listed in Table 3 together with those for ammonia for comparison.

Table 3

A Summary of Amine Properties

Amine	Methylamine	Propylamine	Pyrrolidine	1,2-Propane- diamine	1,3-Propane- diamine	Ammonia
Mol.wt.	31.06	59.11	71.12	74.13	74.13	17.03
B.Pt. °C	-6.45	47.8	86.5	117.3	135.5	-33.35
		-11		52	68	
		-36		23	39	
F.Pt. °C	-92.5	-83.0	-57.8	-37.2	-12.0	-77.7
V.P. at 20°C mmHg	2250	247	49.9	8.0	2.8	6500
S.G. at 20°C	1.07 (air = 1) 0.6845gm/ml for liq. at 1.86 °C	0.7183	0.852(22.5°C)	0.8640	0.8881	0.587 (air = 1)
Viscosity at 20°C C.P.				1.6	1.9	0.18
Surface Tension dynes/cm	19.19 at 20°C		29.6	31.9 at 25°C		21

Table 3 - Continued

Amine	Methylamine	Propylamine	Pyrrolidine	1,2-Propane diamine	1,3-Propane diamine	Ammonia
Crit.Temp. °C	156.9	223.8				132.9
Crit.Pres. atm.	73.6					112.2
Heat of Vaporization Btu/lb at 1 atm	360	218	286	222	119	589.4
Number of Exchangeable H atoms	2	2	1	4	4	3
Wt/Exch. H atom	15.5	29	71	19	19	5.7
References	a), c), d)	b), d)	d)	b), d)	b), d)	a), c), d)

- a) Matheson Gas Data Book
b) Alkyl and Alkylenes Amines, Union Carbide Chemical Company. Copyright 1959, 1961
c) Methylamines, Physical Properties and Analytical Methods, Rohm and Haas Company
d) Atomic Energy of Canada Limited Memorandum "Summary of Amine Properties".

2-3 Properties and Handling of Alkali Metals and Alkali Metal Amides

Alkali metals comprise group 1A of the periodic system; lithium, sodium, potassium, rubidium, cesium and francium. Except for francium, the alkali metals are all soft, malleable materials that display a bright metallic luster when freshly cut. Their melting point and boiling point become lower with increasing atomic weight. The specific gravity increases with, but less rapidly than, the atomic weight. They are the most strongly electro positive of the metals. Within the group, the basicity increases with atomic weight, that of cesium being the greatest.

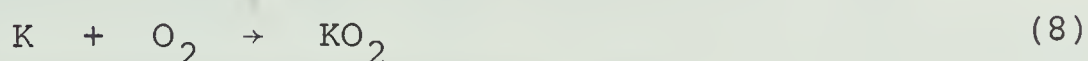
Sodium is easily cut with a heavy spatula or a knife. Potassium is slightly harder than sodium, but rubidium and cesium are softer. Lithium is the hardest of the alkali metals.

Upon contact with air, and particularly with moist air, they take on a dull coating of oxide, hydroxide or carbonate. For this reason, they are preferably stored and handled in the absence of air. The rate and extent of reaction with oxygen varies with the individual alkali metals. Lithium is not attacked by dry oxygen (18), but when contacted with moist air it forms a surface coating that is largely lithium monoxide.



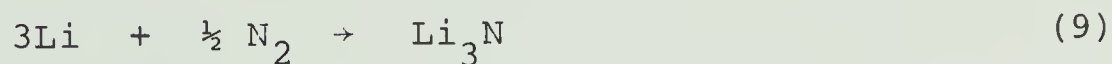
However, unlike other alkali metals, lithium does not form a peroxide with oxygen at atmospheric pressure (19).

Potassium reacts slowly with dry air and rapidly with moisture-containing air to produce some monoxide along with larger amounts of peroxide and superoxide (18).



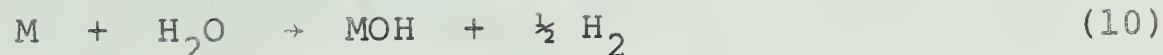
Potassium peroxide, K_2O_2 , is quite unstable and readily oxidized to superoxide KO_2 in air. Potassium superoxide reacts explosively with metallic potassium, hence potassium that is heavily coated with oxide should be handled with great care and should never be cut with a spatula, since this action could easily bring the metal and its superoxide into intimate contact (18).

Lithium is the only alkali metal that reacts readily with nitrogen, forming a reddish-brown nitride (18).



Therefore lithium must be handled under helium or argon rather than under nitrogen.

Perhaps the most characteristic reaction of the alkali metals is that of liberating hydrogen on treatment with water.



Potassium, rubidium and cesium interact with water with such violence that in the presence of air it is virtually impossible to prevent the hydrogen generated from igniting. Sodium may be added in small pieces to large volumes of water below 40°C without adverse effect. Lithium reacts slow enough with water so that no ignition occurs if the temperature is held near room temperature (18).

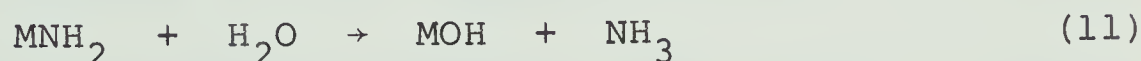
The alkali metals react similarly with alcohols, yielding alcohoxide. The reaction is less vigorous than that with water, but presents an additional hazard in that the alcohols themselves are flammable (18). However, they do not react with saturated hydrocarbons and aromatic hydrocarbons and can be stored or handled in these hydrocarbons. Table 4 (20) summarizes important chemical properties of the alkali metals.

Table 4

Chemical Properties of Alkali Metals

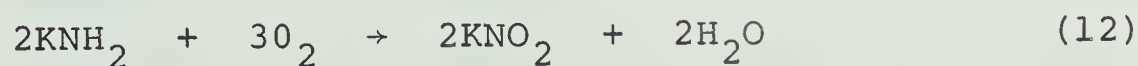
	O ₂	N ₂	H ₂	H ₂ O	C	NH ₃	Halogen F, Cl, Br, I	H ₂ SO ₄
Li	No reaction below 100°C	Reacts	Reactive above 180°C	Slow reaction	Reacts to form Li ₂ C ₂ at high temp.	Slow reaction to form LiNH ₂	Very rapid reaction when exposed to light	Conc; slow reaction Dilute; vigorous reaction
Na	Reactive	No reaction	Reactive above 300°C	Fast reaction	Reacts to form Na ₂ C ₂ at 800- 900°C	Reacts to form NaNH ₂	F: Ignites Cl: Reacts Br: Slowly reacts I: No reaction	Conc; Rapid reaction Dilute; Vigorous reaction
K	Reactive	No reaction	Reactive above 300°C	Very fast reaction	Does not form carbonate	Reacts to form KNH ₂	F, Cl: Very rapid reaction Br, I: Explosive reaction	Explosive reaction
R _b	Burns in air	No reaction	Reactive above 600°C	Very fast reaction	Does not form carbonate	Reacts to form R _b NH ₂	Very rapid reaction	Explosive reaction
C _s	Burns in air	No reaction	Slowly reactive above 600°C	The most vigorous reaction	Does not form carbonate	Reacts to form C _s NH ₂	The most rapid reaction	Explosive reaction

The alkali metal amides are white crystalline solids which melt to clear liquids, frequently tinged slightly yellow or green (21). They are hydrolyzed vigorously by water according to the following equation,

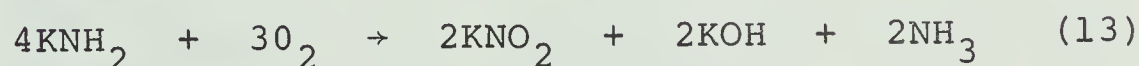


where M is an alkali metal.

Potassium amide is rapidly oxidized on exposure to the atmosphere (22).



As the water formed reacts with potassium amide, the overall reaction is represented by,

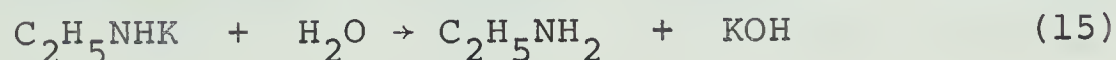


The formation of potassium oxide and the occurrence of a yellow color are reported (23) during the oxidation of potassium amide by dry oxygen. The development of a yellow color is also observed with sodium amide when exposed to the atmosphere. It has been reported that care should be taken with the yellow substance because it is very explosive (24).

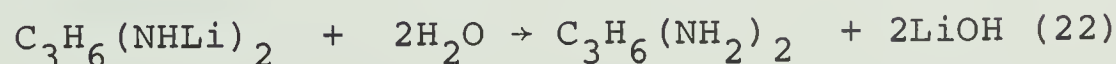
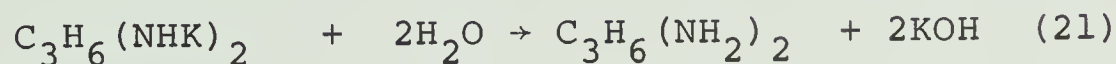
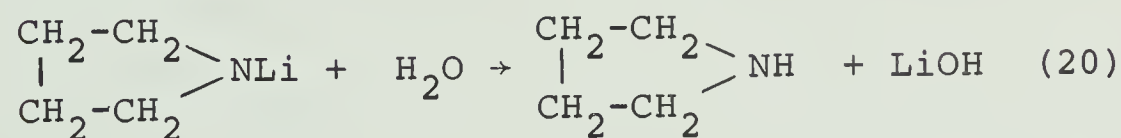
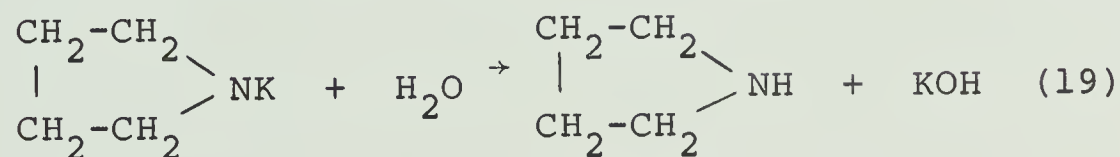
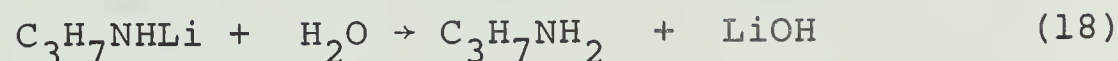
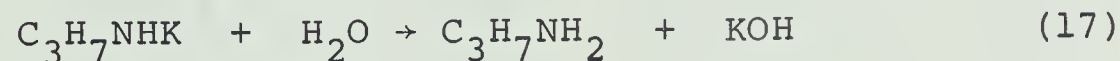
Knowledge of the physical constants of the amides (25) is very limited as shown in Table 5.

No information on the properties of the metal amides derived from amines was found in the literature

except that lithium methyllamide and potassium ethyllamide gave the corresponding amines on hydrolysis (7).



Similar to the above reactions, metal amides of amines most likely undergo the following hydrolysis reactions.



The above reactions form the basis for the method of determining the solubility of amides in amines.

Table 5

Physical Constants of Alkali Amides

<u>Amide</u>	<u>Melting Point</u> °C	<u>Density</u> $d_{40}^{25^{\circ}}$	<u>Heat of Solution</u> K cal/mol	<u>Heat of Formation</u> K cal/mol
LiNH ₂	373-375	1.18	56.3 ± 0.2	42
NaNH ₂	208	1.39	61.4 ± 0.05	27
KNH ₂	338	1.64	64.9 ± 0.15	27
RbNH ₂	309 ± 1	2.58	66.4 ± 0.1	26
CsNH ₂	262 ± 1	3.43	67.0 ± 0.2	28

2-4 Preparation and Solubility of Potassium Amide

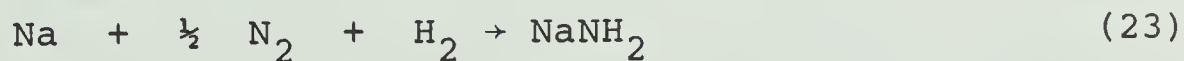
Potassium amide, which has become increasingly important as a reagent in the field of organic synthesis (25), is an effective catalyst (26,27) for the exchange of deuterium between hydrogen and ammonia. Its preparation, properties and uses have been reviewed at length (21, 25, 28). However, it is not possible to purchase this compound from chemical suppliers because it is difficult to avoid deterioration during storage. Therefore, when it is desired in any amount, it must be prepared in a laboratory. The same applied to sodium amide until 1946 (25). However sodium amide and lithium amide are now commercially available.

There are several ways to prepare the alkali amide:

- 1) The reaction of gaseous ammonia with molten metals
- 2) The reaction of liquid ammonia with dissolved metals
- 3) The synthesis directly from the elements
- 4) The electrolysis of salt solutions in liquid ammonia
- 5) As by-products of the reducing action of the alkali metals on organic compounds in liquid ammonia

The reaction of gaseous ammonia upon molten metals is the best way to obtain the alkali amides in quantity. The reaction proceeds in the temperature range of 350-360°C for sodium amide and the reaction time largely depends upon the rate at which the ammonia is admitted (29). However, there is a limit on the kind of materials which can be used for the reaction vessel. Vessels of glass and porcelain are rapidly attacked by the melt and most metals are similarly attacked to a greater or lesser degree (30). Vessels of nickel appear to be the most generally useful for the conversion of metal to amide. Convenient arrangements of apparatus for carrying out this synthesis are described in several references (29,30,31,32,33,34).

An example of synthesis from the elements is given by Sakurazawa and Hara (35) for the preparation of sodium amide.



The above reaction is possible at a pressure greater than 30-50 atm. and at a temperature of 350-450°C. Under the most favorable condition (50 atm., 350°C) 93 percent of the metallic sodium is converted to sodium amide.

The electrolysis of a salt solution in liquid ammonia is reported in several places (36,37,38,39). The electrolysis of potassium bromide in liquid ammonia was

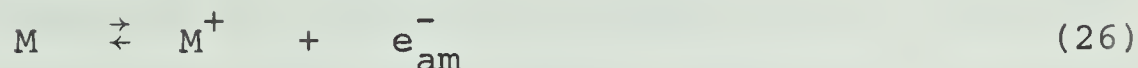
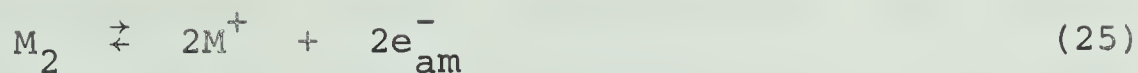
carried out successfully by Akhumov and Druzyakova (36) using 6-10 volts.



A yield of 80-99 percent of potassium amide was obtained.

The reaction of liquid ammonia with dissolved alkali metal seems to be the most practical method in a laboratory. This method is especially convenient for studying the solubility of the alkali amide in amines since the liquid ammonia can be easily evaporated off leaving the product and no elaborate procedures are needed to prevent contamination during transfer of the obtained amide into a desired solvent.

The alkali metals, lithium sodium, potassium, rubidium and cesium, dissolve in liquid ammonia and such solutions all possess a characteristic deep blue color in the dilute concentration range. The absorption spectra of the blue solutions all exhibit an intense band around 15,000 Å (40, 41), indicating that some common component in such systems is responsible for this color (42). It is generally agreed that when the metal dissolves it dissociates to some extent to give metal ions and electrons, both of which are solvated. The two equilibria considered to be present are (10):



Monomer M may be considered a simple ion pair in which the ammoniated metal ion and ammoniated electron are held together by Coulmbic forces. Similarly dimer M_2 may be considered a quadrupolar ionic assembly of the two ammoniated metal ions and the two ammoniated electrons. The solvated electron is represented by e_{am}^- . Although these solutions are very stable at low temperature, the reaction of the metal with ammonia to form the amide becomes noticeable after long periods of contact or at more elevated temperatures.



Joannis (43) observed no appreciable formation of amide with sodium and potassium solutions at $-78^\circ C$. Ruff and Geisel (44) claim that at room temperature, half saturated solutions require the lapse of the following times before they are completely decomposed to give amides. Cs, 1-2 hours, Rb, 6-10 hours, K, 2-3 days, Na and Li, 2-3 weeks. Joannis (43) reports that, in a closed system, the pressure of the hydrogen resulting from conversion of the alkali metal to the amide has an inhibiting effect upon the rate of the reaction but Kraus (45) denies this statement by showing that the pressure increases in

a closed system at a nearly constant rate. More recently, it was revealed (9) that the decomposition of the solution is dependent upon the initial condition of its preparation. The relatively large initial rate of decomposition as determined by measurement of the hydrogen pressure has been attributed to a reaction of metal with strongly adsorbed water on the glass reactor surface. When the adsorbed water is removed by the reaction with the solution, a more stable system results.

The reaction of alkali metals with liquid ammonia is greatly influenced by catalysts. Whereas a solution of potassium in liquid ammonia may be preserved for a couple of days even at room temperature, in the presence of iron oxide or finely divided platinum the potassium is completely converted to potassium amide within an hour and often in a few minutes. This catalyzing effect is less with sodium and lithium. Many metals, and metallic oxides and hydroxides serve to catalyze these reactions. Burgess and Kahler (46) studied this catalytic effect and determined the most appropriate catalysts, using both foils and powders. For various foils, the times in minutes for the conversion of 5-6 mg of potassium in 50 ml of liquid ammonia to amide are: platinized platinum, 2.6; rusted iron, 3.1; nickel, 21; pure iron, 44; smooth platinum, 66; zinc, 71-86; copper, 102-232; silver, 245-258; gray platinum, 556; tantalum and niobium, 1000; no catalyst, over 1500. Platinized

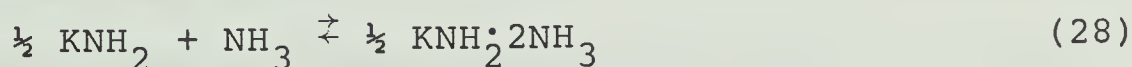
platinum, rusted iron and nickel were the most efficient of foils, while ferrous oxide and ferric oxide were the best powdered catalyst. They also observed that sodium amide in solution poisoned the catalyst, while potassium amide did not change its effectiveness. Ferric oxide has been widely used by the investigators (67,47) studying the deuterium exchange reaction. Some of them (48) report that a stainless steel reactor vessel will catalyze the reaction. The metal amides also catalyze the reaction, thus the decomposition of the alkali metal - ammonia solution is self catalyzed once the reaction starts (8). The completion of the reaction can be directly observed by a change in color of the solution from a deep blue to a pale yellow or colorless solution (27).

Considerable uncertainty about the actual solubility of potassium amide in liquid ammonia existed until Moreau and Lepoutre (49) and Schenk and Tulhoff (50) reported results which are in fairly good agreement. Some early authors (51) reported values which were too low, i.e. 3.6 gm KNH_2 in 100 gm of NH_3 at 25°C . This probably resulted from the incomplete saturation of the liquid ammonia. Regrettably, this value has been adopted by many of the investigators of the deuterium exchange reaction.

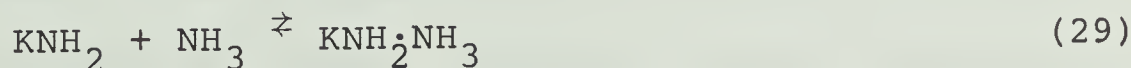
Schenk and Tulhoff (52) obtained the solubility data together with the aspects of crystallization over the temperature range of -50.5 to -32.4°C . Later they reported values down to -75°C (50). Their experimental apparatus

was a glass vessel divided into two parts and provided with a sintered glass filter so that solid-free saturated solutions could be obtained by turning the vessel upside down. Solubility diagrams for the systems, $\text{NaNH}_2/\text{NH}_3$, $\text{RbNH}_2/\text{NH}_3$, and $\text{CsNH}_2/\text{NH}_3$ were also obtained. The characteristic nature of the system KNH_2/NH_3 is that it precipitates two different ammoniates; $\text{KNH}_2\cdot\text{NH}_3$ and $\text{KNH}_2\cdot 2\text{NH}_3$ while other systems precipitate the amide itself or mono-ammoniate. The relative order of the magnitude of the solubility is: $\text{RbNH}_2 > \text{CsNH}_2 > \text{KNH}_2 > \text{NaNH}_2$. The two types of ammoniate of the potassium amide were first found by Juza and Mehne (53,54). Their tensimetric measurements of the system KNH_2/NH_3 concluded that below -60°C , $\text{KNH}_2\cdot 2\text{NH}_3$, from -60 to -42°C , both $\text{KNH}_2\cdot 2\text{NH}_3$ and $\text{KNH}_2\cdot\text{NH}_3$, and above -42°C , $\text{KNH}_2\cdot\text{NH}_3$ respectively precipitate. Moreau and Lepoutre (49) also agree on this phenomena and add that above -17.7°C the precipitate is KNH_2 itself. Thus in the solution, the following equilibria are established:

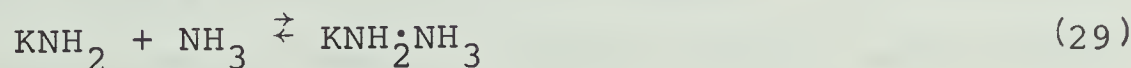
Below -60°C



From -60° to -42°C



Above -42°C



The enthalpy of formation for each reaction is:

ΔH_1	= -7.3 (54)	-8.2 (49)	-7.2 (50)	Kcal/mole NH_3
ΔH_2	= -9.4	-11.3	-9.2	"
ΔH_3	= -8.3	-	-7.0	"

ΔH_1 , ΔH_2 , and ΔH_3 represent the enthalpy of formation for the reactions (28), (29) and (30) respectively. Moreau and Lepoutre (49) present the following empirical equations for the solubility as a function of temperature.

From -78.8 to -42.2°C

$$\log_{10} \{x(1-x)^2\} = 7.400 - 1964.2/T \quad (31)$$

From -42.2 to -17.7°C

$$\log_{10} \{x(1-x)\} = 2.155 - 732.8/T \quad (32)$$

Above -17.7°C

$$\log_{10} x = -0.113 - 120.3/T \quad (33)$$

where x is a mole fraction of potassium amide in liquid ammonia and T is the absolute temperature. These equations agree pretty well with the experimental data of their own and of Schenk and Tulhoff (50,52). Reported solubilities of potassium amide in liquid ammonia are shown in Figure 1.

There is no information on the solubility of the potassium amide in amines. Humphreys (14,15) reports that the alkali metal amide reacts with primary alkyl or cycloalkyl amines with by-product ammonia. This reaction could be employed to obtain aliphatic alkali metal amide.

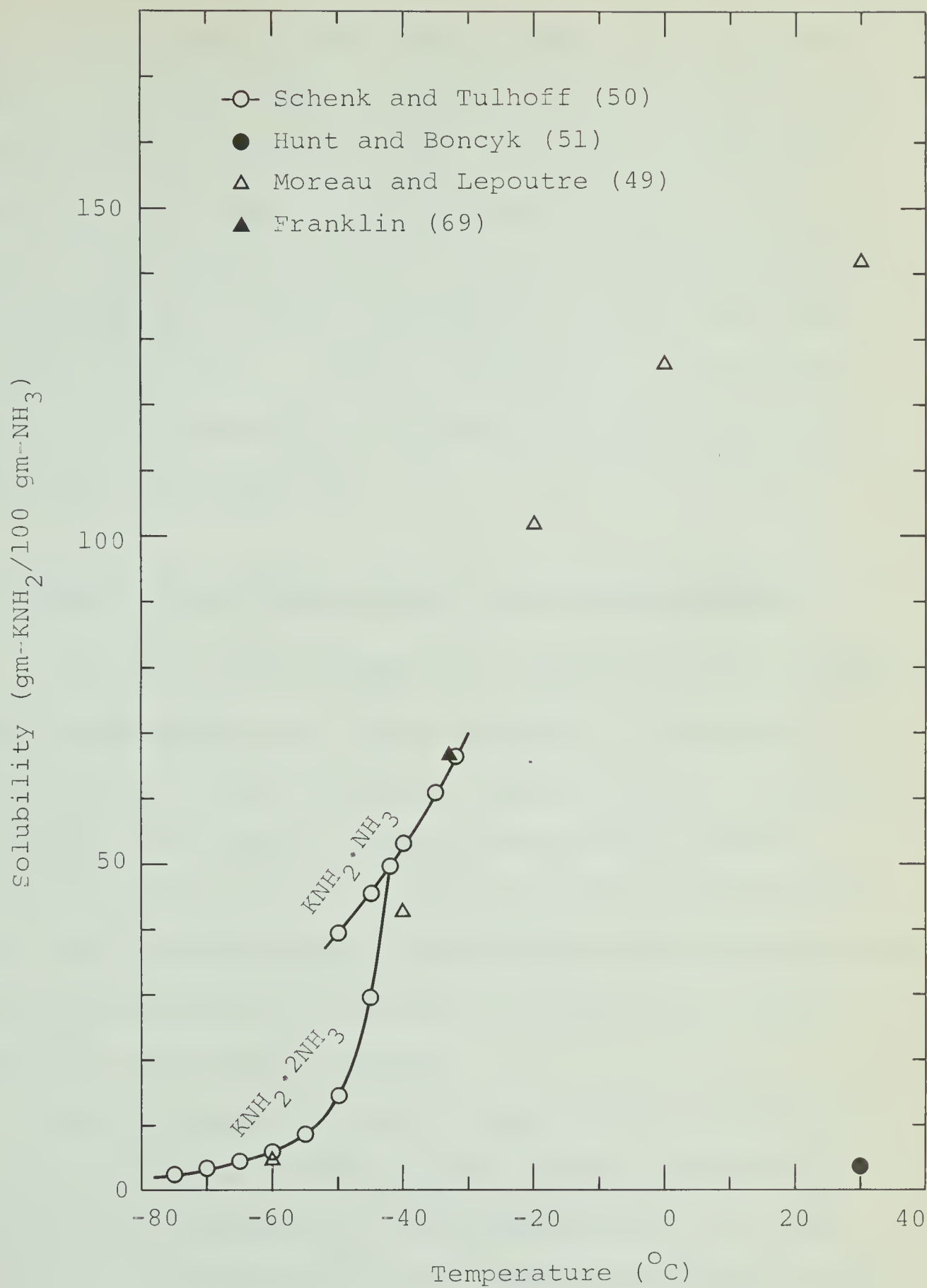


Figure 1. Solubility Diagram of Potassium Amide in Ammonia

Sodium amide is much less soluble (50) in liquid ammonia (0.095 gm NaNH_2 in 100 gm of NH_3 at -35°C) and lithium amide is insoluble (55). This may be the main reason for their lower catalytic activities for the deuterium exchange reaction, since the catalyzing species are believed to be the free amide ion NH_2^- and the undissociated amide MNH_2 . Linear dependence of the exchange rate on the concentration of potassium amide and sodium amide has been shown (7).

2-5 Solubility of Alkali Metals in Aliphatic Amines

Audrieth and Kleinberg (11) report that the solvent power of the amines for ionic compounds is inferior to that of their parent substance, liquid ammonia. Moreover, the ability to dissolve inorganic substances usually decreases markedly with increasing length of hydrocarbon chain. The simpler primary monoamines and diamines possess to a limited extent the ability to dissolve the alkali metals to yield blue solutions.

Early studies (45,56,57) report that lithium and cesium are soluble in methylamine, whereas sodium and potassium are insoluble in this medium when it is completely free from ammonia (58). Kraus (45) observed that lithium was more soluble in ethylamine than in methylamine, but that it was insoluble in propylamine. He showed that potassium was soluble in 1,2-ethanediamine but that the

solution was very unstable (decomposed to form amide), that potassium and sodium were insoluble in ethylamine and that lithium, sodium and potassium were insoluble in secondary and tertiary amines. More recently Birch and McDonald (59) have supported the fact that the alkali metals are insoluble in these amines.

Later works (40,60,61,62,63,64) on the alkali metal - amine solutions are mostly concerned with the measurements of electron spin resonance spectra, optical absorption spectra and electrical conductivities. These studies have been carried out in an attempt to describe the nature of the metal - amine solutions as compared to that of metal - ammonia solutions. From these investigations, it has been shown that all the alkali metals are soluble in methylamine and 1,2-ethanediamine and that lithium, sodium and potassium are soluble in ethylamine and 1,2-propanediamine. Although the resulting solutions all have a blue color, the absorption spectra of these solutions differ from one metal to the other. Dye and Dewald (65) propose a general model to describe the nature of metal - amine solutions based on the information from the above studies. Three types of species in the solutions are suggested:

- 1) solvated electrons similar to those in metal - ammonia solutions
- 2) covalent dimers, similar to those existing in the gas phase for the alkali metals

- 3) combination of a solvated molecule ion, M_2^+ ,
with an electron trapped in the field of this
ion

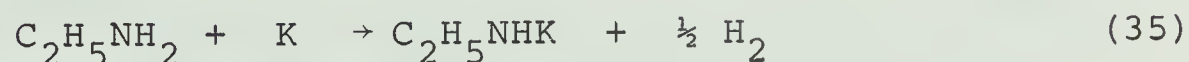
Evers et al (66) and Dewald and Dye (67) studied the electrical conductance of the metal - amine solutions as a function of metal concentration and reported the solubility for two amines. In 1,2-ethanediamine, lithium: 0.287 mol, sodium: 2.39×10^{-3} mol, potassium: 1.04×10^{-2} mol, rubidium: 1.31×10^{-2} mol, and cesium: 5.4×10^{-2} mol per liter of the amine, and in methylamine, lithium: 5.26 mol per liter of the amine at room temperature.

Most of the above authors took care to take measurements while the prepared solutions were fresh, since decomposition of the solution took place to some extent after long standing. Fowles et al (61) observed that sodium and potassium formed much more stable solutions than did lithium. Potassium and sodium solutions generally decomposed to form amides over a period of 6-12 hours, while lithium solution was stable for only 25-30 minutes. The rapid decomposition of the lithium solution can probably be attributed to impurities in the metal. (Potassium and sodium were distilled in vacuum prior to use, while lithium was cut under benzene since the high melting point of lithium made the vacuum distillation difficult.)

2-6 Preparation and Solubility of Aliphatic Alkali Amides

Some of the aliphatic alkali metal amides are prepared by the reaction of an alkali metal with aliphatic amines, similar to the reaction of the alkali metal with liquid ammonia. However, not all the amines react directly with the alkali metal to form amide.

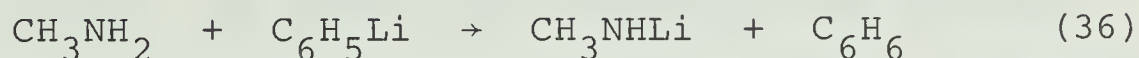
Bar-Eli and Klein (7) successfully converted methylamine and ethylamine to lithium methylamide and potassium ethylamide respectively by direct contact of the metal with the amine.



Ferric oxide was employed to catalyze the reactions. No experimental details are given for these reactions. They found experimental difficulty in dissolving alkali metals, other than lithium, in amines. Thus, they dissolved potassium amide in methylamine to obtain potassium methylamide instead of preparing it by the reaction of potassium with the amine. However, only part of the potassium amide was converted into potassium methylamide. Their reported saturation concentration of the lithium methylamide in methylamine at -22°C is about 0.01 mole per 1000 gm of the solution. However this value was not obtained by attempts to saturate the solution, but was determined from the plot of the rate of exchange of deuterium with the

methylamine against the concentration of the lithium methylamide. The exchange rate increases in proportion to the catalyst concentration and it flattens out at the concentration, 0.01 mole/1000 gm solution. They interpreted this fact as the saturation of the solution with the catalyst. They report that the observation of the saturation of the solution is difficult because of the turbidity in the solution caused by traces of lithium hydroxide. No comment is made on the saturation solubility of potassium ethylamide in ethylamine.

One of the most frequently used methods of making the aliphatic alkali amide consists of treating the amine with a compound such as phenyllithium in ether. Luthy et al (68) obtained the methyl lithium amide by this method.



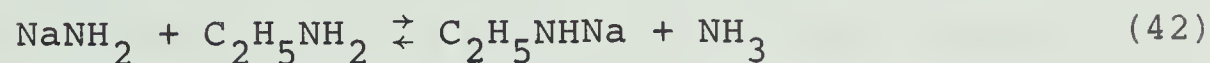
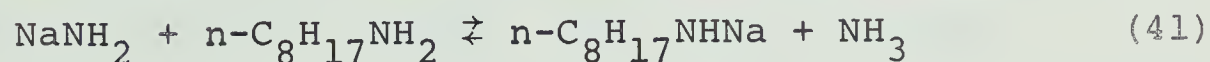
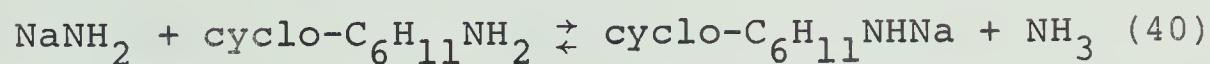
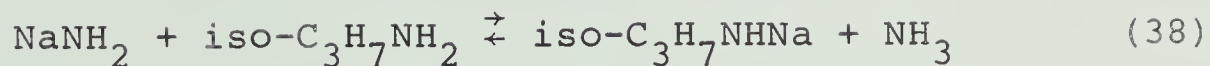
The phenyllithium was firstly prepared by adding bromobenzene dropwise to an anhydrous ether in which freshly cut, thin slices of lithium were suspended. The resulting phenyllithium solution in ether was introduced to an ether solution of anhydrous methylamine. The lithium methylamide was formed with some evolution of heat and formation of a creamy precipitate. Lithium cyclohexylamide (16), lithium diethylamide and lithium

ethylphenylamide (17) can be prepared in a similar way. The solution of lithium cyclohexylamide in cyclohexylamine was clear and of a pink color. It was observed that contamination with air resulted in a yellow solution. No examples of the preparation of potassium compounds by the above type of reaction could be found in the literature.

Another method that can be employed is the reaction of alkali metal amide with amines. Although the lower aliphatic amines were not believed to react with potassium or sodium amide (21), Humphreys (14, 15) found that an alkali metal amide reacts with primary alkyl or cycloalkyl amines with by-product ammonia.



Where M is an alkali metal and R is an alkyl or cycloalkyl group. He states that secondary and tertiary amines do not form the corresponding amides. However, the above reaction is reversible and does not convert all the alkali metal amide to the corresponding aliphatic alkali amide unless the ammonia evolved is fully removed from the system. The reactions carried out were:



The experimental conditions were given for the first two reactions. Sodium iso-propylamide and sodium butylamide were obtained by the continuous removal of ammonia for about 60-120 hours at temperatures of 50-100°C. The purity of the resulting products varied from 87 to 96 percent. Again, no information on the preparation of potassium amides by this method is available.

No other information on the preparation and solubility of amides of the amines of interest in the study undertaken here was found in the literature.

3. EXPERIMENTAL

3-1 Equipment

Figure 2 is a schematic drawing of the equipment that was assembled for the determination of amide solubilities in aliphatic amines. The system includes amine purification units A and B, a reaction vessel C and a sampling unit D. All vessels are constructed from pyrex glass and their approximate sizes are: A, 300 ml., B, 600 ml., C, 150 ml., D, 10 ml.

The system was connected to a vacuum pump (Welch Duo-seal) and all experiments were carried out in an atmosphere of dry helium. The cartesian manostat G was used to maintain a constant low pressure in the system.

Temperature control of the reaction vessel was accomplished by a low temperature bath which contained a mixture of n-propanol and dry ice. This maintained the temperature between -78 and -77°C . It was clear and colorless when fresh, thus direct observation of the reactor contents was possible.

The double jacketed condenser E was used to condense the amine distilled from the purification units and to condense amine vapor generated during the preparation of amide solutions. The coolant for the condenser was trichloroethylene which was cooled in a low temperature bath before entering the condenser. The condenser was able to reach -60°C .

Symbols for Figure 2

A,B:	Amine Purification Vessel
C:	Reaction Vessel
D:	Sampling Unit
E:	Condenser
F:	12/30 Glass Joint
G:	Cartesian Manostat
H:	Recycle Pump
J,K,L:	Low Temperature Bath
M ₁ ,M ₂ :	Manometer
N:	Sample Bottle for Mass Spectrometry
O:	Liquid Nitrogen Trap
P,Q:	Stopper
S ₁ -S ₁₄ :	High Vacuum Stop Cock

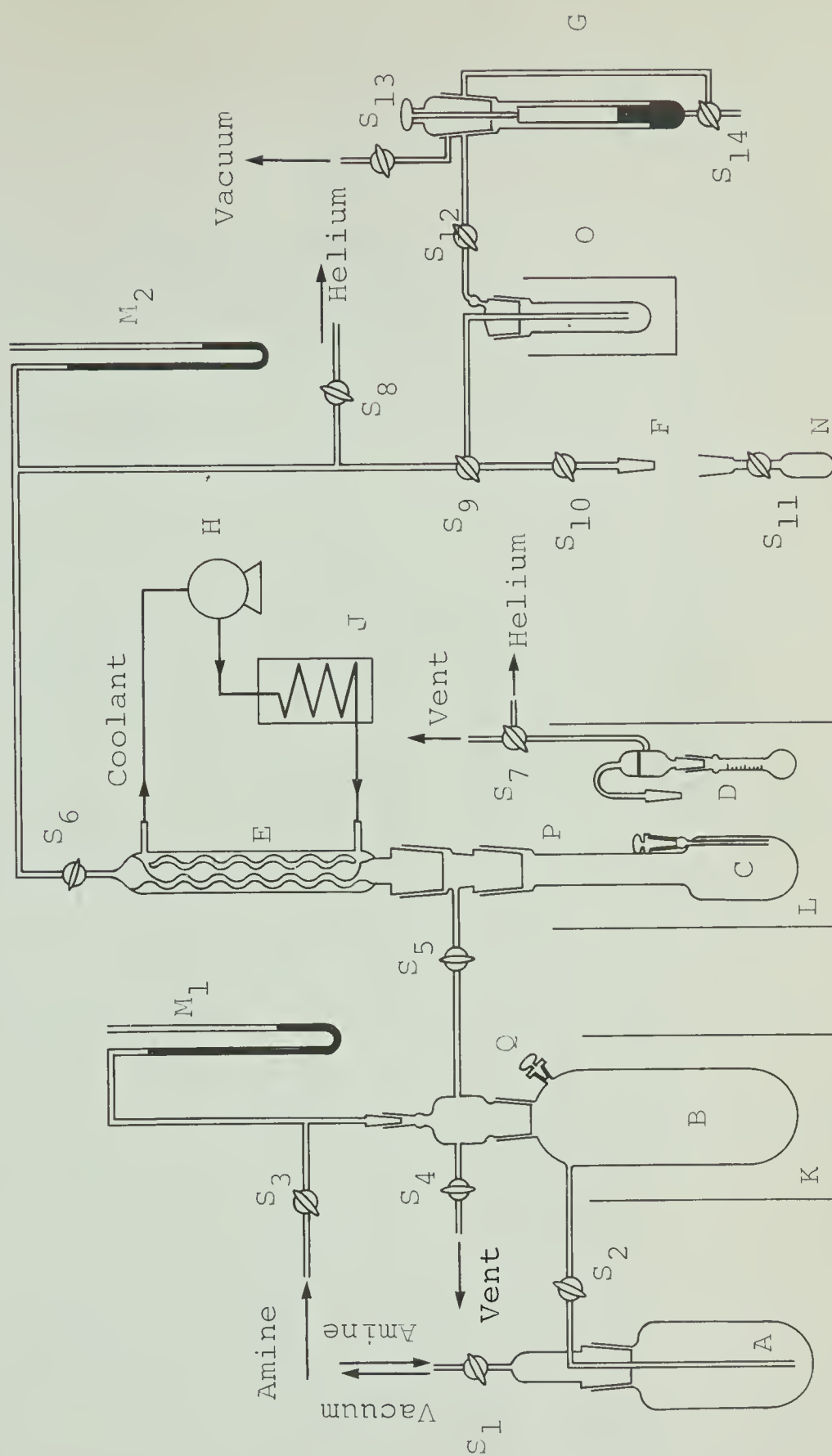


Figure 2. Schematic Drawing of Equipment

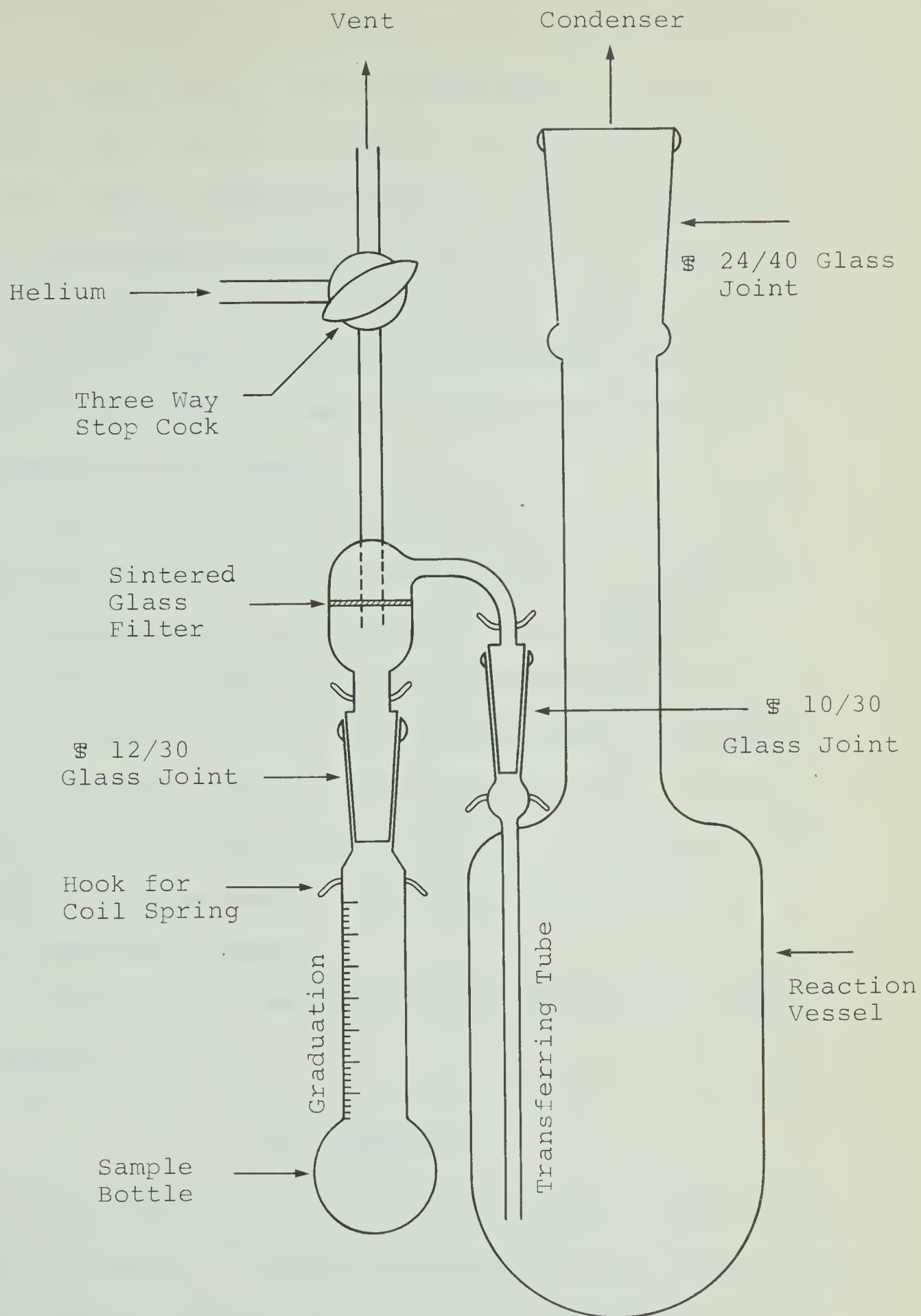


Figure 3. Reaction Vessel and Sampling Unit

The recycle pump used was an Eastern 316 SS Type 103 centrifugal pump. Trichloroethylene is such a strong solvent that it dissolves many of the plastic materials used in the construction of less expensive pumps. Polyethylene tubing was used for the circulating line because it is not attacked by trichloroethylene. Coolants such as methanol and ethanol are not suitable since they become too viscous to recycle at the operating temperature.

The sintered glass filters of 10-20 μ and 4-8 μ were interchangeably used in the sampling unit. According to the manufacturer's specification, the former is designed for filtration of crystalline precipitates while the latter is for a coarse bacterial filtration.

The glass socket joint F was used for a vacuum source for drying the sample solution. It was also used to take an off-gas sample during the reaction of an alkali metal with amines.

The reaction vessel and sampling unit are shown in Figure 3.

3-2 Materials

The materials of importance and their source are listed in Table 6. The purities and the major impurities in the amines used for the solubility studies are tabulated in Table 7. Although the amines were of the highest

commercially available grades, they contained significant amounts of dissolved water and thus had to be dried prior to their use. The basic drying procedures adopted in this work are described in 3-3-(A).

Table 6

A List of Materials and Their Source

<u>Compound</u>	<u>Source</u>
Ammonia	Matheson
Methylamine	Matheson
Propylamine	Eastman Organic Chemicals
Pyrrolidine	J.T. Baker Chemical
1,2-Propanediamine	J.T. Baker Chemical
1,3-Propanediamine	J.T. Baker Chemical
Benzene	McArthur Chemical, Reagent Grade, Thiophene Free
n-Propanol	Standard Chemicals
Trichloroethylene	Fisher Scientific
Potassium	Fisher Scientific
Lithium	Fisher Scientific
Lithium Amide	Lithium Corporation of America
Ferric Oxide	Fisher Scientific, Reagent Grade
Molecular Sieves 4A	Fisher Scientific
Silicone Grease	Dow Corning

Table 7

Amine Purity and Major Impurities

<u>Compound</u>	<u>Purity wt. %</u>	<u>Major Impurities</u>
Methylamine	98.0	Water 0.8% Max. Dimethylamine 0.8% Max. Trimethylamine 0.6% Max.
Propylamine	98.0*	Water 1.32%
Pyrrolidine	95.0**	Water 3%**
1,2-Propanediamine	95.0	Water
1,3-Propanediamine	-	Water
Ammonia	99.95	Water 50 p.p.m. Oil 3-5 p.p.m.

Specifications were supplied by the manufacturers listed in Table 6 except the values with * and **.

* Union Carbide Chemical Company

** Ansul International Corporation

3-3 Experimental Procedures

The following (A), (B), (C) and (D) describe general experimental procedures. Additional operational procedures are given in the section on the results of experiments.

(A) Purification of Amines

Water was removed from ammonia and methylamine by contacting them with small pieces of lithium in vessel B. They dissolve the lithium and form blue solutions very quickly and any contained water should be converted to lithium hydroxide before the lithium is converted to the amide. Therefore, the ammonia or methylamine evaporated from this solution should be free from water.

Propylamine, pyrrolidine, 1,2-propanediamine and 1,3-propanediamine were dried by contacting them with 4A molecular sieves prior to using the procedure described above. This was necessary because these amines contain a relatively large amount of water, and large amounts of lithium do not readily dissolve in them. Approximately 40 grams of 1/10" pellets of 4A molecular sieves were introduced to vessel A and heated for 24 hours at 200°C under vacuum. Then the amine of interest was charged to A and left to contact with the sieves for at least 10 hours. Then this amine was transferred to B for additional drying with lithium. Drying during this step was

improved for some amines by using powdered lithium. This was obtained by dissolving lithium in ammonia and then evaporating off the ammonia.

Dissolved gases in the amines were removed during the condensation of the amine vapor in E.

(B) Amide Preparation

An alkali metal freshly cut in benzene was charged to the reaction vessel C while its surface was wet with the benzene. The benzene was then removed under vacuum. In preparation for potassium amide, potassium methyllamide and lithium methyllamide, a few milligrams of ferric oxide were introduced as a catalyst before the charge of the metal. For the amides of other amines, however, no catalyst was used.

For the initial runs, potassium was distilled into the reaction vessel, however, it was difficult to introduce sufficient potassium to saturate the solution by this method.

Recycle of the coolant was started and the desired system pressure set by the cartesian manostat. This was normally a few inches of mercury lower than atmospheric pressure. The reaction vessel C was immersed in the low temperature bath and the amine - lithium solution in B heated so that amine vapor condensed in the condenser was transferred to vessel C. After approximately half of vessel C was filled with amine, the heating of the solution in B

was stopped. The reaction mixture in C was allowed to heat up to the boiling temperature of the amine, thus increasing the rate of reaction.

(C) Sampling

When the reaction was complete, the stopper P was quickly replaced with D. Then both C and D were immersed in the same low temperature bath and held in it at least for two hours to ensure equilibrium. By applying a helium pressure of about 6 inches of mercury, a portion of the solution in C was forced into the sample bottle through the sintered glass filter. The sample bottle had been previously calibrated and supplied with graduations so that the volume of sample could be directly determined. More than one sample could be obtained from a given charge in vessel C by attaching another sample bottle while flushing D with helium. Each sample size thus taken was from seven to twelve milliliters.

The off-gas from the reaction was collected in an initially evacuated mass spectrometric sample bottle at about one inch of mercury.

(D) Analysis

The sample was transferred to an Erlenmeyer flask and dried. The remaining solid was hydrolyzed by adding distilled water, the amine formed by hydrolysis was removed and then the amount of alkali hydroxide formed was

determined by titration with hydrochloric acid. The end point of titration was determined by phenolphthaleine color indicator.

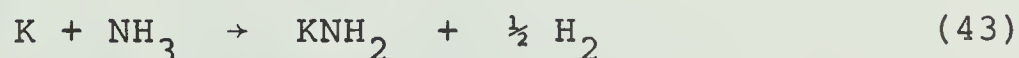
Drying of ammonia and methylamine solutions was accomplished by boiling them in a fume hood. The solutions of higher boiling amines were dried either under vacuum or by heating them in an oven. Vacuum drying was carried out to observe the nature of the solid in sample solutions.

3-4 Experimental Results

The experimental results are summarized in Table 8. Details of results for each of the systems studied are given in the following sections.

(A) Solubility of Potassium Amide in Liquid Ammonia

Potassium amide was prepared by contacting metallic potassium with liquid ammonia in the presence of a few milligrams of ferric oxide as a catalyst. Approximately one to two grams of potassium was cut under mineral oil, cleaned with benzene and charged to the reaction vessel. Removal of the benzene by vacuum left a dry metal whose surface was silvery, but which was partly covered with a blue film. Approximately 100 ml of dry liquid ammonia was transferred to the reaction vessel and the metal readily dissolved in the ammonia to form a deep blue solution. The reaction,



occurred at the boiling point of the solution, about -33°C , in one or two hours. This was indicated by a change in color of the solution from deep blue to colorless or slightly yellow. The color change was only noticeable during the latter stages of the reaction. The catalyst which was initially reddish-brown turned black. However, only a very small amount was present so that it did not interfere significantly with visual observation of the

Table 8
A Summary of Solubility Study

	Potassium	Lithium	Potassium Amide	Lithium Amide
Ammonia	Reacts to form KNH_2 Catalyst: Fe_2O_3 Solubility 11.3 gm $\text{KNH}_2/1.\text{sol'n. at}$ -77°C		Solubility ≈ 11.8 gm $\text{KNH}_2/1.\text{sol'n.}$ at -77°C .	
Methylamine	Reacts to form CH_3NHK . Catalyst Fe_2O_3 . Solubility ≈ 38 gm $\text{CH}_3\text{NHK}/1.$ $\text{sol'n. at } -77^\circ\text{C}$	Reacts to form CH_3NHLi . Catalyst Fe_2O_3 . Solubility appears large, may be more than 123 gm $\text{CH}_3\text{NHLi}/1.\text{sol'n. at}$ -77°C . Solubility characteristics complicated.	Solubility ≈ 2.8 gm $\text{KNH}_2/1.\text{sol'n.}$ at -77°C .	Almost insoluble
Propylamine	Insoluble	Reacts to form $\text{C}_3\text{H}_7\text{NHLi}$. Reaction slow with metal pieces. Powdered lithium reacts rapidly. Solubility ≈ 33 gm $\text{C}_3\text{H}_7\text{NHLi}/1.$ $\text{sol'n. at } -77^\circ\text{C}$	Solubility ≈ 0.39 at -78°C , 0.44 at 24°C gm $\text{KNH}_2/1.$ sol'n.	Insoluble

Table 8 (continued)

	Potassium	Lithium	Potassium Amide	Lithium Amide
Pyrrolidine	Insignificant reaction, metal stays shiny	Reactions to form $\begin{array}{c} \text{C}-\text{C} > \text{NLi} \\ \\ \text{C}-\text{C} \end{array}$ Solubility \approx 51 gm $\text{C}_4\text{H}_8\text{NLi}$ / 1. soln. at 22°C	Solubility \approx 2.0 gm KNH_2 / 1. soln. at 24°C	
1,2-propanediamine	Very slow reaction metal stays shiny but its surface becomes porous	Reacts to form amide. Titration impossible with color indicator	Solubility \approx 2.9 gm KNH_2 / 1. soln. at 24°C	
1,3-propanediamine	Very slow reaction metal stays shiny but its surface becomes porous	Reacts to form amide. Solubility \approx 48.4 gm $\text{C}_3\text{H}_6(\text{NHLi})_2$ / 1. soln.	Solubility \approx 7.6 gm KNH_2 / 1. soln. at 20°C	

solution. In each run, no solid potassium amide was observed in the solution because of its large solubility at this temperature. Reported solubilities (49,50) indicate that more than 40 grams of potassium would have been required to saturate the solution at this temperature. However, when the solution was cooled to -78°C and held at this temperature for a few hours, white needlelike crystals which were about 1 to 3 mm long precipitated. These were probably $\text{KNH}_2 \cdot 2\text{NH}_3$ as reported by Moreau and Lepoutre (49) and Schenk and Tulhoff (50,52). Samples of the solution were filtered through a 10-20 μ sintered glass filter. The ammonia was boiled off from the sample in a fume hood at room temperature, leaving a fair amount of white solid some of which had a yellow tinge. This solid was decomposed by the addition of distilled water. The ammonia evolved in hydrolysis in accordance with equation (11) was removed by boiling the solution for about two hours. After cooling to room temperature, the resulting potassium hydroxide solution was titrated with 0.1 N HCl. Table 9 shows the measured solubilities. Results from initial runs did not agree with these values and this was found to be due to incomplete saturation of the solution.

The potassium amide reacts violently with water and it often explodes. Therefore, extreme care must be taken when decomposing it with water. The technique employed here was to add the water dropwise with a syringe if the

quantity of amide was small. The potassium amide remaining in the reaction vessel was decomposed by first covering it with benzene and then adding water slowly while vigorously shaking the vessel contents. Any potassium amide which had a yellow color was particularly explosive and extra caution was required in disposing of it.

Table 9

Measured Solubility of KNH_2 in Ammonia

<u>Run No.</u>	<u>Temp. °C</u>	<u>Solubility gm-KNH_2/l.soln.</u>
(A) -5	-78	11.8 12.2
(A) -6	-78	10.3 11.0 10.7
	-77	12.3 12.2 12.2
(A) -7	-77	10.7 10.3 10.5
(A) -8	-78	11.8 11.9 12.2
(A) -9	-78	11.4 11.7 11.8

(B) Solubility of Potassium in Methylamine

Potassium dissolved into methylamine very slowly at -78°C with a blue-color slowly rising from its surface. At the boiling point of the solution, (about -6.5°C), it dissolved a little faster and turned the solution from colorless to deep blue. However, the rate at which the metal dissolved was still very slow. It took nearly one day to dissolve approximately 0.9 gm of potassium into about 100 ml of the amine at its boiling point and at atmospheric pressure. The gas evolved during the solvation was continuously removed from the reaction vessel. Mass spectrometric analysis determined this off-gas as hydrogen. Therefore the formation of potassium methyllamide is considered to take place while the metal dissolves.



At the last stage of the potassium solvation, the solution turned pale yellow and a blue color existed near the small piece of the metal that remained. When all the metal dissolved, a clear pale yellow solution was obtained. It became paler when cooled to -78°C .

A small amount of ferric oxide was added to initiate the decomposition reaction. It again turned black at the end of the reaction. A more rapid solvation and reaction of potassium was observed in the presence of

larger amounts of catalyst, but the catalyst then interfered with visual observation of the color of the solution.

The solubility of potassium methylamide in methylamine was fairly large even at -78°C , and solutions prepared as described above had to be concentrated by a factor of approximately four by evaporating the amine from the solution before a white flaky solid precipitated.

Samples of the solution were taken through a $4-8\mu$ filter. Filtered samples were clear, pale yellow solutions. When they were exposed to air, the yellow color became more intense. Drying of these samples by evaporating off the amine in a fume hood left a large amount of white solid which had a yellow tinge. This solid was hydrolyzed by the addition of distilled water. Both the water and the methylamine which was evolved in hydrolysis were removed by heating the solution to dryness. The white solid which remained was assumed to be potassium hydroxide. It was dissolved in distilled water and titrated with 0.5 N HCl. The solubility reported as grams of CH_3NHK per liter of the solution is given in Table 10.

The potassium methylamide reacted violently with water. Therefore it was treated in a manner similar to that for potassium amide for decomposition and disposal.

Table 10

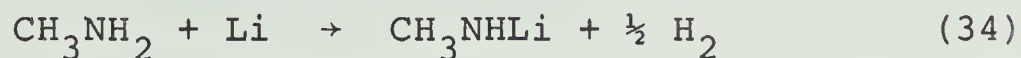
Measured Solubility of CH_3NHK in Methylamine

<u>Run No.</u>	<u>Temperature °C</u>	<u>Solubility gm-CH_3NHK/l.soln.</u>
(B)-3	-77	35.5 38.4 38.8
(B)-7	-78	31.8 32.7 30.5

(C) Solubility of Lithium in Methylamine

Lithium dissolved in methylamine much faster than potassium to form a deep blue solution. This solution was fairly stable at its boiling point, about -6.5°C . Evaporation of the amine left a fine powdered silvery metal. However, when a sufficient quantity of ferric oxide catalyst, approximately 10-20 mg, was added, a reaction occurred which turned an initially blue solution into a milky gray solution which then became clear except for significant amounts of turbidity. Some difficulty was encountered in initiating the reaction with a few milligrams of ferric oxide and because of this the amount of the catalyst was increased. The dark color of the solution was probably due to the catalyst since its original reddish-brown color disappeared and a black solid was observed when the reaction was complete.

The gas given off during the reaction was analyzed by mass spectrometry and was found to be hydrogen. This would indicate that the following reaction occurs.



Attempts were made to filter the solution through a 10-20 μ filter but a cloudy filtrate was obtained. Thus filtration was tried with a finer filter, 4-8 μ , but samples still often remained somewhat dark and turbid. The darkness of the sample differed each time. It was more intense when a black material was forced into the transferring tube along with liquid, indicating that the filter could not trap all of this material.

The drying of a sample left a gray solid, which on hydrolysis gave a slightly dark solution. This hydrolysis reaction was not as vigorous as that of potassium methyllamide. Table 11 shows the measured solubilities at -77°C. The quantity of lithium added was increased for each run. The solubilities account quantitatively for the quantity of lithium added and the degree of turbidity did not appear to be proportional to the quantity of the lithium added. The behavior of the lithium in the solution appears to be quite complex in that when a solution of the concentration given for Run No. (C)-16 was allowed to stand for 36 hours, five different liquid phases were observed. The bottom phase was dark in that it contained

Table 11

Measured Solubility of CH_3NHLi in Methylamine

<u>Run No.</u>	<u>Solubility at -77°C gm-CH_3NHLi/1.soln.</u>	<u>Remarks</u>
(C)-13	21.8 19.6	Clear, no darkness
(C)-14	34.8 35.0 38.8	Slightly dark and turbid
(C)-15	87.0 86.6	Slightly dark and turbid
(C)-16	123.0 123.0	Slightly dark and turbid Li charge ≈ 1.2 gm If all the metal dissolved, expected solubility was approximately 128 gm CH_3NHLi /1.soln.

some black solid and the other phases were clear with some turbidity. This turbidity is difficult to explain, but it does not appear to be associated with the lithium methylamide. It may be caused by traces of lithium hydroxide as suggested by Bar-Eli and Klein (7), impurities in the metal and by the presence of the Fe_2O_3 catalyst. The results obtained suggest that lithium methylamide is very soluble in methylamine. It was practically impossible to treat more than two grams of lithium in a vessel of the size of this study. Thus further attempts to determine the saturation solubility were not made.

Cutting of lithium in benzene was rather difficult because of its hardness and took a relatively longer time than for potassium. Surface contamination during this time was inevitable. When the metal was dried in the reaction vessel, small amounts of white and black material deposited as a thin film on the lithium.

(D) Solubility of Potassium Amide in Methylamine

Potassium amide was prepared by the method described in section 3-4-(A). After ammonia was removed under vacuum, the white dry solid KNH_2 was contacted with methylamine solution in vessel B. The runs that left a partly yellow colored KNH_2 were discarded. This methylamine solution of potassium amide was boiled for one hour to stir the solution well and dissolve the solid quickly and also attain the following equilibrium.



Generation of ammonia was not directly observed. The solution was at first white and turbid but when the solid settled on the bottom of the vessel it became clear and almost colorless. The solution was cooled to -78°C and kept at this temperature for about two hours and then sampled. The presence of the white solid on the bottom ensured the saturation of the solution. When the sample was taken to dryness under vacuum, it left a small amount of white solid which was assumed to be potassium

amide partly converted to potassium methylamide. The solid was decomposed by addition of distilled water. The ammonia and methylamine evolved in this hydrolysis (equations (11) and (16)) were removed by boiling the solution for about two hours. After cooling to room temperature, the resulting potassium hydroxide solution was titrated with 0.1 N HCl. Table 12 shows the measured solubilities reported as gm-KNH₂ per liter of the solution.

Table 12
Measured Solubility of KNH₂ in Methylamine

<u>Run No.</u>	<u>Temperature °C</u>	<u>Solubility gm-KNH₂/l.soln.</u>
(D) -2	-77	2.39 2.86 2.53
(D) -3	-77	3.05 3.38 3.24
(D) -6	-78	2.83 2.91 2.77
	-77	2.81 2.77
(D) -8	-77	2.71 2.89
(D) -10	-78	2.98 3.23 3.22

(Filter: 4-8μ)

(E) Solubility of Lithium Amide in Methylamine

Lithium Amide was purchased from Lithium Corporation of America. This white solid was almost insoluble in the amine. When the sample was dried under vacuum, there was no visible amount of solid left. However, titration with HCl required approximately 0.05 ml of 0.1 N HCl. This in turn indicated that not more than 0.01 gram of LiNH_2 was soluble in a liter of the amine at -78°C .

(F) Solubility of Potassium in Propylamine

Potassium was contacted with dry propylamine at room temperature. Except for a few small bubbles released from the metal surface, no appreciable change took place after contacting for 12 hours. Ferric oxide was then added but no change occurred after an additional six hours of contacting.

Finely divided potassium was prepared using the method described for lithium in 3-3-(A). However this potassium still did not dissolve in the amine after contacting for 5 hours at room temperature. The amine was found immiscible with a concentrated solution of potassium in ammonia.

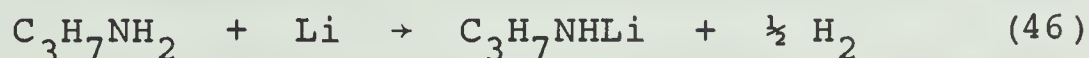
(G) Solubility of Lithium in Propylamine

When lithium was contacted with dry propylamine at atmospheric pressure and room temperature, small bubbles were continuously released from the metal for

more than a week. However, a blue color was not observed at these conditions. Bubble release may be due to the surface reaction of lithium with the amine to form amide and the metal solvation rate may be too slow to turn the solution blue.

Powdered lithium however readily dissolved in the amine forming a deep blue solution. Almost immediately, this blue solution began to turn milky white and a suspension of white solid was observed. A light purple color was seen as an intermediate color in the above color change. When the white solid settled, a clear colorless solution was obtained. Filtered samples were also clear and colorless, but they soon turned yellow when exposed to air.

The off-gas from the reaction was found to be hydrogen. Therefore, the following reaction is thought to occur.

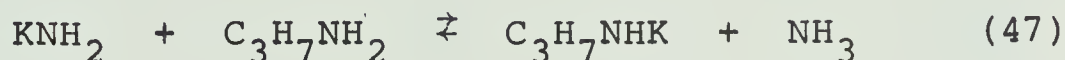


Drying of the sample under vacuum left a fair amount of yellow solid. This yellow color essentially disappeared following the hydrolysis procedure. The solid dissolved in distilled water quickly and formed a pale yellow solution. When this solution was dried again, white solid, probably lithium hydroxide, was obtained. Thus titration with phenolphthaleine color indicator was possible. The

measured solubility of lithium propylamide in propylamine was 29 gm- $\text{C}_3\text{H}_7\text{NHLi}$ /l.soln. at 23°C and 33 gm- $\text{C}_3\text{H}_7\text{NHLi}$ /l.soln. at -77°C .

(H) Solubility of Potassium Amide in Propylamine

Distilled propylamine is a colorless liquid. Upon contact with potassium amide, it formed a white, turbid solution and when the solid settled a clear, pale yellow solution remained. In the meantime, a small portion of the white potassium amide turned to a yellow flocculent solid. This might be potassium propylamide resulting from the following equilibrium.



However, the generation of ammonia was not observed. Filtered samples were pale yellow. Drying under vacuum left a trace of yellow solid. This solid reacted with distilled water generating gas bubbles. In the first several runs, solubilities scattered very much, i.e. from 0.44 to 2.7 grams of KNH_2 per liter of the solution at -78°C . Thus it was suspected that the water in the amine had not been fully removed and the resulting potassium hydroxide was interfering with the determination of the solubility. Therefore, the amine was dried with molecular sieves prior to drying with lithium pieces. The solubilities thus obtained were reasonably reproducible and agreed with the lowest

values of the previous runs. Measured solubilities are listed in Table 13.

Table 13
Measured Solubility of KNH_2 in Propylamine

<u>Run No.</u>	<u>Temperature °C</u>	<u>Solubility gm-KNH_2/l.soln.</u>
(H) -11	27	0.398 0.461 0.442
(H) -12	-78	0.398 0.348 0.423
	24	0.448 0.427

(Filter: 4-8 μ)

One sample taken at room temperature was cooled to -78°C but no visible precipitate was observed. Actually the measured solubility at -78°C was essentially the same as that measured at room temperature. Because of the very low solubility, a blank test using only amine and water was carried out to ensure that some other factor was not interfering with the titration. The amine - water mixture did not leave any solid when dried and did not respond to the phenolphthaleine color indicator.

(I) Solubility of Lithium Amide in Propylamine

Lithium amide was contacted with propylamine at room temperature and at atmospheric pressure. No visible change occurred and titration showed that this material is insoluble in the amine.

(J) Solubility of Potassium in Pyrrolidine, 1,2-Propanediamine and 1,3-Propanediamine

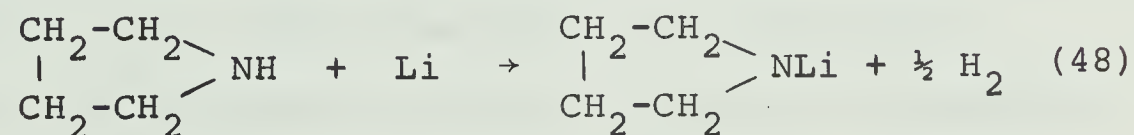
Pyrrolidine as obtained from the supplier had a pale yellow color but when it was dried and distilled, a clear colorless liquid was obtained. The shipped 1,2- and 1,3-propanediamines were clear and colorless liquids. The distillation of these amines was carried out under vacuum since their vapor pressures are very low.

Potassium metal remained shiny in all three amines. Observation of the metal in pyrrolidine was made for three days under atmospheric pressure and room temperature. After this time, the metal was still shiny and the amine was clear and colorless. On the other hand, when potassium was contacted with the diamines at the same condition, a faint blue color along with the formation of bubbles on the metal surface was observed. The solution remained colorless but in a few days the metal appeared porous on the surface, indicating that the potassium is slowly dissolving and at the same time reacting with the diamines. The solution was sensitive to air and picked up a brown-dark brown color quickly

when exposed to the atmosphere. Because of very slow solvation and reaction, no further attempts were made to prepare the saturated solutions.

(K) Solubility of Lithium in Pyrrolidine

Lithium dissolved slowly in pyrrolidine and formed a blue solution at room temperature. This blue solution turned into a creamy colored solution without any catalyst. A blue color was observed near the metal until it all dissolved. A suspension of white solid existed in the solution. Gas given off during the reaction was analyzed by mass spectrometry and found to be hydrogen. Therefore, similar to the reaction of lithium with simpler amines, lithium pyrrolidine is considered to form according to the following reaction:



Samples were taken at room temperature. They were also creamy colored solutions which turned to yellow-brown when exposed to the atmosphere. Cooling of the sample to -40°C did not precipitate any visible solid. Drying of one sample solution under vacuum left a large amount of brown sticky solid. This solid dissolved in distilled water to form a yellow solution. Subsequent drying and resolution in distilled water

failed to remove this yellow color. Titration of four samples from one run using phenolphthaleine indicator gave the following indicated solubilities; 52.2, 53.1*, 51.1, 50.1 grams of lithium pyrrolidine per liter of the solution at 22°C.

(L) Solubility of Lithium in 1,2-Propanediamine

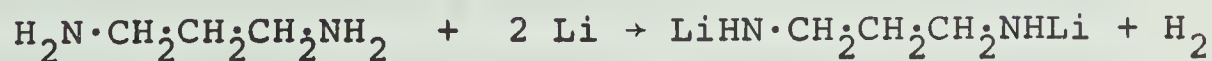
All 0.9 gm of lithium dissolved into approximately 100 ml of 1,2-propanediamine in 6 hours at room temperature forming a deep blue solution. At the same time, the decomposition of the solution occurred with generation of hydrogen. The solution turned light gray immediately after all the metal dissolved and appeared viscous and somewhat gelatinous. The amine was distilled off to concentrate the solution by a factor of two but the solution still maintained the same appearance and became more viscous. It was difficult to tell if solid was suspended in the solution. Attempts were made to filter a sample from this solution through a 4-8 μ filter. The filtered sample was still gray and may have contained some suspended material.

* (Sample dried under vacuum prior to adding distilled water. For others, distilled water was added to the sample solutions without vacuum drying).

When a sample of this solution was exposed to air it became initially green, then yellow, then brown and finally very dark brown. A large amount of very dark brown solid was obtained when the sample was dried under vacuum. This dark brown color remained after hydrolysis and could not be removed by repeated drying and solution in distilled water. Titatration using a color indicator was not possible. However, subsequent experiments showed that if water is added to a partially dried sample solution prior to exposing it to air, a white precipitate can be obtained. This white precipitate is thought to be lithium hydroxide.

(M) Solubility of lithium in 1,3-Propanediamine

A blue solution of lithium in 1,3-propanediamine was also obtained at room temperature. The time required for all of 0.8 gm of lithium to dissolve in approximately 100 ml of the amine at 25°C was approximately 8 hours with continuous degassing of the reaction vessel. The decomposition of the solution took place with generation of hydrogen in parallel with the metal solvation. The decomposition was assumed to be the formation of dilithium 1,3-propanediamide represented by the following equation.



The rate of the solvation decreased markedly with increase of the system pressure. The blue color was predominant in the solution at the vapor pressure of the solution but it was confined to a small area near the metal piece at atmospheric pressure. When the blue color disappeared, a light gray, viscous and somewhat gelatinous solution was obtained. Samples taken at room temperature were clear and colorless but became yellow when exposed to air. This color change was not as marked as for 1,2-propanediamine solution.

Addition of distilled water to the sample gave a pale yellow solution which, when dried, left a fair amount of white solid, probably lithium hydroxide. The solubility measured at 25°C was 48.4 grams of dilithium 1,3-propanediamide per liter of the solution.

After the sample was taken, dry oxygen was passed over the solution in the reaction vessel. This turned the solution yellow-brown quickly.

(N) Solubility of Potassium Amide in Pyrrolidine,
1,2-Propanediamine and 1,3-Propanediamine

Both pyrrolidine and 1,2-propanediamine formed pale yellow solutions when contacted with potassium amide at room temperature. On the other hand, 1,3-propanediamine exhibited a reddish-brown color at the beginning of contact and gradually turned to yellowish-brown. Solubility of potassium amide in these three

amines appeared low and most of the potassium amide charged remained white on the bottom of the reaction vessel.

Samples were taken through a 4-8 μ filter after at least 5 hours of contact. Drying of the sample of pyrrolidine solution left a small amount of yellow sticky solid, while the samples of 1,2- and 1,3-propanediamine solutions left a dark brown also sticky solid. However, all of these solids gave yellow solutions on hydrolysis and, when they were taken to dryness again, the color almost disappeared and white solid was obtained. This white solid was assumed to be potassium hydroxide. Thus titration with phenolphthaleine color indicator was possible. The indicated solubilities were 2.0 gm-KNH₂/l.soln. at 24°C, 2.9 gm-KNH₂/l.soln. at 24°C and 7.6 gm-KNH₂/l.soln. at 20°C for pyrrolidine, 1,2-propanediamine and 1,3-propanediamine solution respectively.

Air contamination occurred in all the samples to a greater or lesser degree when they were exposed to the atmosphere. Pyrrolidine solution turned from pale yellow to brownish yellow 1,2-propanediamine exhibited a dark greenish-brown color and 1,3-propanediamine picked up a dark brown, almost black color. When dry oxygen was contacted with 1,3-propanediamine solution a dark brown solution was very quickly formed.

Blank tests on the three amines were carried out to ensure that any alkali detected by the titration with HCl was coming from the metal amides and not from the amines themselves. When the mixtures of amines and water were dried in an oven, they left a trace of brown material. But this material did not respond to phenolphthaleine color indicator.

4. DISCUSSION

4-1 Equipment

Experimental difficulties encountered resulted mainly from the fact that the experiments had to be carried out in the absence of air. The following were the main problems:

(1) Air leaks from groundglass joints

Amines slowly dissolved vacuum grease and formed narrow channels where air could leak through. Thus, ground glass joints and stopcocks had to be cleaned and re-greased often to prevent leaks.

(2) Contamination by air during sampling procedure

After a saturated solution had been prepared in the reaction vessel, the stopper P had to be replaced with the sampling unit. At this time, the top portion of the solution in the transferring tube was exposed to air for a short time. However, this replacement could be accomplished fairly quickly and the open space to the air was so small that no appreciable contamination was observed during this step. However, it was difficult to prevent air contamination when the initial sample bottle was exchanged for a second bottle. The system was flushed with helium during the transfer process but some contamination was inevitable. For ammonia, methylamine and propylamine solutions, contamination during this step was not

severe, but for solutions containing pyrrolidine, 1,2- and 1,3-propanediamine, the contamination was rather quick and sometimes the color change invaded into the main solution through the transferring tube. Some closing device, such as a stopcock, between the sample bottle and the glass filter may help for sampling at room temperature. However, operation of a stopcock at -77°C is virtually impossible.

(3) Plugging

Plugging of the sintered glass filter often occurred after taking a few samples. Washing of the filter by water left a brown color in the filter, indicating that the catalyst powder went into the small pores of the filter and was trapped in them. Solutions prepared without using catalyst, especially lithium in amines, also caused some plugging. This may be due partly to impurities in the metal and partly to air contaminated materials in the filter after taking one or two samples. Increased viscosity of the solution at the lower temperature seemed to enhance plugging.

4-2 Purification of Amines

Amines obtained from the suppliers contained a significant amount of water. Since the reaction of water with alkali metals is very rapid, any water content in an amine would convert a part of dissolved metal to

its hydroxide prior to any formation of amide. The presence of metal hydroxide could thus result in erroneous values of amide solubilities. For some early runs with pyrrolidine, 1,2- and 1,3-propanediamine, the potassium was coated by a film of potassium hydroxide and further reaction to form the amide was prevented.

Drying with 4A molecular sieves appeared successful and the initially encountered interference by the metal hydroxide was not observed.

4-3 Reaction of Alkali Metal with Amines

Monoamines and dissolved alkali metal most likely undergo the reaction generally expressed by the following equation.



This reaction is supported by the following facts; (1) color change of the solution, (2) generation of hydrogen, which was detected by mass spectrometry, (3) existence of an alkaline material after drying the solution. In addition, Bar-Eli and Klein (7) report this type of reaction occurring, reactions (34) and (35). Thus the amines are working as acid to the alkali metal.

The color change of the catalyst from initial reddish-brown to black may be the result of the reduction of ferric oxide Fe_2O_3 to ferrous oxide Fe_3O_4 by the strong reducing action of metal-ammonia solutions and metal-amine solutions.

It is not known whether the alkali amides prepared from diamines are of the type which have two metal atoms in one molecule such as $\text{MHN}-(\text{CH}_2)_3-\text{NHM}$ or of the type where only one metal atom combines with the amine molecule such as $\text{MHN}-(\text{CH}_2)_3-\text{NH}_2$, or whether some of each is formed. In reporting the solubilities found in this work, it has been assumed that both of the amino groups had equal opportunity to react with the metal and that only the diamide was formed.

4-4 Color Phenomena

Solutions of alkali metal in ammonia and amines are blue. The intensity of the color depends on the concentration, the higher the concentration, the deeper the color. As the reaction of the dissolved metal with the amine proceeds, the blue color fades. For several systems, it was observed that after the bulk of the solution had obtained the color of the amide solution

that any small metal piece remaining would still emit a blue color which disappeared after travelling a short distance in the solution. Figures 4,5,6, 7 illustrate this phenomenon. This indicates that the rate at which the dissolved metal is converted into amide competes with the rate at which the metal dissolves. Probably the amide formed is working as a catalyst for the conversion of metal to amide. With some metal-amine mixtures, particularly potassium in 1,2- and 1,3-propanediamine, the metal solvation rate is so slow compared to the rate of amide formation that the blue color is confined to near the surface of the metal.

Solutions of amides in amines generally exhibit a yellow color of varying intensity or are colorless. Traces of impurities in the metal and in the amine appear to result in more intense color. Figure 6 shows 1,2-propanediamine while contacting lithium pieces during the drying operation. The lithium charged was not as clean as that charged in the reaction vessel and may have resulted in the strong yellow color, whereas the solution prepared in the reaction vessel was light gray.

Many of the color changes due to air contamination of the amide solutions are not understood. However, it is certain that the color change is related to the presence of metal amide in the solution since the amine

itself does not undergo similar color changes when exposed to the atmosphere. Oxygen in the air is most likely responsible for the air contamination as was described in sections 3-4-(M) and (N). Streitweiser et al (16) reported that a solution of lithium cyclohexylamide in cyclohexylamine was pale pink but that an air leak changed this color to yellow. They do not offer any explanation for this phenomenon.

4-5 Accuracy of Data and Comparison with Data Reported in the Literature

The solubilities measured exhibited a scatter of generally less than plus or minus six percent. These inconsistencies are thought to be due to the following reasons.

- (1) Impurities in metal
- (2) Air contamination
- (3) Errors in reading sample volume
- (4) Incomplete separation of amide from amine
- (5) Errors in titration

In many cases, the scatter of the solubilities determined from the same sample solution was almost as large as the scatter in the values for different runs. Thus the latter four reasons, (2), (3), (4) and (5) may be the most significant and they are mostly concerned with the analytical procedures. Working

with larger sample volumes would lessen the error in (3), but it would increase the handling difficulty of metal and metal amide. Formation of KNO_2 due to oxidation (reaction (13)) would result in a scatter of the measured solubility. Separation of amide from amine, if it is complete, should give white metal hydroxide after hydrolysis of amide and subsequent drying. However, dried sample often showed a yellow tinge. It has not been confirmed whether this color is due to incomplete separation of amine from the amide or to some impurity in amine. Some brown impurity was observed in blank tests. Titration using a pH meter may be useful when titrations using a color indicator do not give sharp end-points.

The measured solubility of potassium amide in liquid ammonia at -77°C was $11.5 \text{ gm-KNH}_2/\text{l.soln.}$ as a simple arithmetic average. To compare this value with other reported values, the units must be converted to $\text{gm-KNH}_2/100 \text{ gm-NH}_3$. The only density data available for solutions of potassium amide in ammonia are for solutions at -40°C (50), which give a density of 0.885 gm/cm^3 at the saturation concentration. Pure ammonia has a density of 0.690 gm/cm^3 at this temperature and 0.734 at -77°C . Using this information, the density of a saturated solution at -77°C was estimated to 0.741 gm/cm^3 , which did not differ much from that of pure

ammonia. Using this value the solubility of 11.5 gm-KNH₂/100 gm-NH₃ becomes 1.58 gm-KNH₂/100 gm-NH₃. The value reported by Schenk and Tulhoff is 2.2 gm-KNH₂/100 gm-NH₃ at -75°C. The equation (31) presented by Moleau and Lepoutre (49) indicates the solubility of 0.81 gm-KNH₂/100 gm-NH₃ at -77°C. These values appear to be in reasonable agreement. This agreement was thought to indicate that the experimental techniques employed were adequate for the determination of amide solubilities in amines.



Figure 4. Color Photograph of Potassium in Methylamine



Figure 5. Color Photograph of Powdered Lithium in Propylamine



Figure 6. Color Photograph of Lithium in 1,2-Propanediamine



Figure 7. Color Photograph of Lithium
in 1,3-Propanediamine



Figure 8. Color Photograph of Potassium
Amide in 1,3-Propanediamine

5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The determination of amide concentrations in simple amines was generally successful, however, it was not entirely satisfactory for some of the higher boiling amines. Air contamination of samples was sometimes severe and separation of amines from amide was difficult. Other methods of analysis such as flame photometry should be investigated. Avoidance of air contamination should increase the accuracy of the solubility measurements.

The materials handled, especially the alkali metal amides, are very hazardous and care should always be taken during the course of an experimental run. The use of a face mask is strongly recommended.

Potassium was found to be soluble in methylamine and slightly soluble in 1,2- and 1,3-propanediamine. The potassium amides obtained from these solutions were also soluble in the amines. Thus they may be effective catalysts for deuterium exchange between hydrogen and these amines. Potassium methylamide had a relatively large solubility. Potassium is not appreciably soluble in propylamine and in pyrrolidine.

Lithium readily dissolved in most of the amines of interest. However, only finely powdered lithium would dissolve in propylamine. The lithium amides resulting from these solutions also exhibited relatively

large solubilities. They, too, should be of interest as possible catalysts for deuterium exchange.

Potassium amide was found to be slightly soluble in all the amines studied.

Future work could involve,

- (1) The determination of the temperature dependence of the solubilities.
- (2) The determination of the saturated solubility of lithium methylamide in methylamine, dilithium 1,2-propanediamide in 1,2-propanediamine.
- (3) The determination of solubilities of the potassium amides of 1,2- and 1,3-propanediamine in these amines.
- (4) An investigation of the chemistry involved in the reaction of the metal with diamines.
- (5) A study of the chemistry involved in the color phenomena.

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Appendix 1 - Calculations Involved in Titration

1-1 KNH_2 in Ammonia and in Amines

Molecular weight of KNH_2 : 55.13 gm/gm-mol

Sample volume : S_V ml

Titrant volume (0.1N HCl : T_V ml

The hydrolysis of KNH_2 gives the equivalent moles of KOH which is titrated by 0.1N HCl. In T_V ml of the titrant,

$$0.1 \times T_V/1000 = T_V \times 10^{-4}$$

moles of HCl exists. The same moles of KNH_2 are present in S_V ml of the sample solution. Therefore, in a liter of the sample solution, there exists,

$$T_V \times 10^{-4} \times 1000/S_V = T_V/S_V \times 10^{-1}$$

moles of KNH_2 . In a unit of grams of KNH_2 in a liter of the solution, molecular weight is multiplied to give,

$$T_V/S_V \times 10^{-1} \times 55.13 = T_V/S_V \times 5.513 \text{ gm-}\text{KNH}_2/\text{l.soln.}$$

1-2 LiNH_2 in Amines

Molecular weight of LiNH_2 : 23.06 gm/gm-mol

In the similar way with 1-1, we obtain,

$$T_V/S_V \times 2.306 \text{ gm-LiNH}_2/\text{l.soln.}$$

1-3 CH_3NHK and CH_3NHLi in Methylamine

Molecular weight of CH_3NHK : 69.15 gm/gm-mol

Molecular weight of CH_3NHLi : 36.99 gm/gm-mol

Therefore, we have,

$$T_v/S_v \times 6.915 \text{ gm-CH}_3\text{NHK/l.soln.}$$

$$T_v/S_v \times 3.699 \text{ gm-CH}_3\text{NHLi/l.soln.}$$

1-4 $\text{C}_3\text{H}_7\text{NHK}$ and $\text{C}_3\text{H}_7\text{NHLi}$ in Propylamine

Molecular weight of $\text{C}_3\text{H}_7\text{NHK}$: 97.20 gm/gm-mol

Molecular weight of $\text{C}_3\text{H}_7\text{NHLi}$: 65.04 gm/gm-mol

Resulting equations are,

$$T_v/S_v \times 9.720 \text{ gm-C}_3\text{H}_7\text{NHK/l.soln.}$$

$$T_v/S_v \times 6.504 \text{ gm-C}_3\text{H}_7\text{NHLi/l.soln.}$$

1-5 $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad \quad \quad \diagup \\ \text{CH}_2-\text{CH}_2 \end{array} \text{NK}$ and $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad \quad \quad \diagup \\ \text{CH}_2-\text{CH}_2 \end{array} \text{NLi}$ in Pyrrolidine

Molecular weight of $\text{C}_4\text{H}_8\text{NK}$: 109.21 gm/gm-mol

Molecular weight of $\text{C}_4\text{H}_8\text{NLi}$: 77.05 gm/gm-mol

$$T_v/S_v \times 10.921 \text{ gm-C}_4\text{H}_8\text{NK/l.soln.}$$

$$T_v/S_v \times 7.705 \text{ gm-C}_4\text{H}_8\text{NLi/l.soln.}$$

1-6 $\text{CH}_3\text{-CH(NHK)-CH}_2\text{-NHK}$ and $\text{CH}_3\text{-CH(NHLi)-CH}_2\text{-NHLi}$ in 1,2-Propanediamine and $\text{KHN-CH}_2\text{-CH}_2\text{-CH}_2\text{-NHK}$ and $\text{LiHN-CH}_2\text{-CH}_2\text{-CH}_2\text{-NHLi}$ in 1,3-Propanediamine

Molecular weight of $\text{C}_3\text{H}_8\text{N}_2\text{K}_2$: 150.31 gm/gm-mol

Molecular weight of $\text{C}_3\text{H}_8\text{N}_2\text{Li}_2$: 85.99 gm/gm-mol

Since these amines contain two atoms of K or Li, they produce two moles of KOH or LiOH by hydrolysis of one mol.

Therefore, the resulting equations are,

$$T_V/S_V \times 7.50 \quad \text{gm-C}_3\text{H}_8\text{N}_2\text{K}_2/\text{l.soln.}$$

$$T_V/S_V \times 4.30 \quad \text{gm-C}_3\text{H}_8\text{N}_2\text{Li}_2/\text{l.soln.}$$

Appendix 2 - Density of Liquid Ammonia

In order to compare the solubility in liquid ammonia reported in various units, one must know the temperature dependence of the density of liquid ammonia.

The International Critical Table (Vol. 3, p. 23) presents the following equation for the density of liquid ammonia.

From -78°C to -33°C

$$d_4^t = 0.6386 - 1.34 \, t \times 10^{-3} - 1.365 \, t^2 \times 10^{-6}$$

Computed values from this equation are given in Figure 9 together with the values listed in the reference (8).

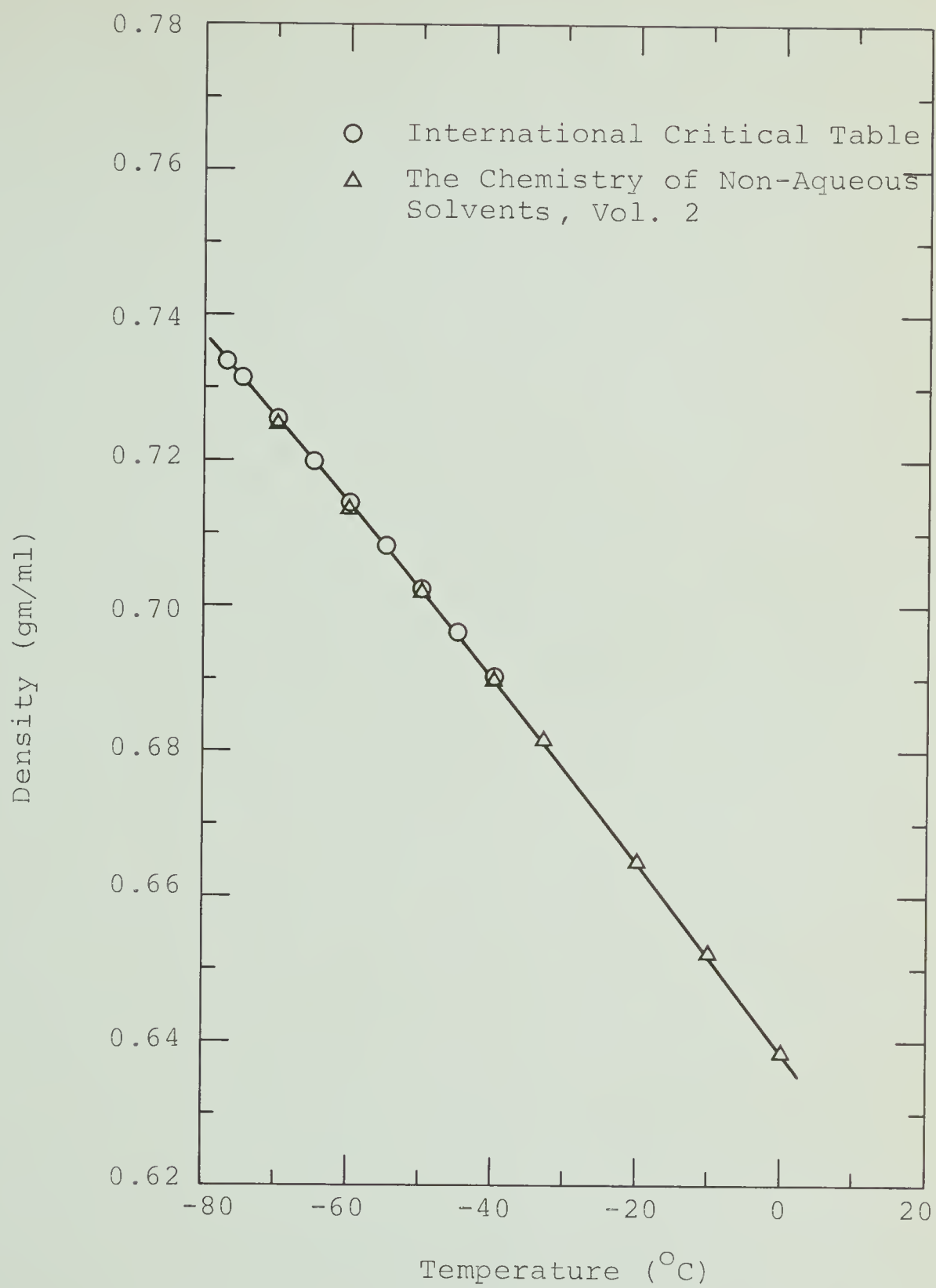


Figure 9. Density of Liquid Ammonia

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